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ENCAPSULATED DECON FOR USE ON MEDICAL PATIENTS

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NOTICES

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The Office of Public Affairs has reviewed this report, and it is releasable to the National Technical Information Service, where it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for publication.

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Encapsulated -OCl⁻ materials (bleaches) and chemical warfare agent (CWA) indicators have been developed and evaluated for use as a skin decontamination material for wounded and incapacitated personnel. More than 40 capsule samples were prepared, and the twelve best were evaluated using live agents. The -OCl⁻ materials selected as capsule core were calcium hypochlorite and sodium dichloroisocyanurate dihydrate. Cellulose acetate butyrate (CAB) and chlorinated rubber were the candidate polymers that worked best as capsule wall materials. Both -OCl⁻ materials effectively neutralized HD, but neither fully neutralized GB nor GD. Dibromo-dimethyl-hydantoin (DBDMH) was found to be a useful indicator for HD as well as effective decon for HD. Luminol and indole were studied as indicators for GB and GD respectively. Those showed some promise but will require considerably more development. Three capsule samples were evaluated with each agent in pig skin tests. With HD, capsules significantly reduced agent penetration. With GB, one capsule system prevented any further penetration of the skin sample by agent. With GD, capsules appeared not only to prevent

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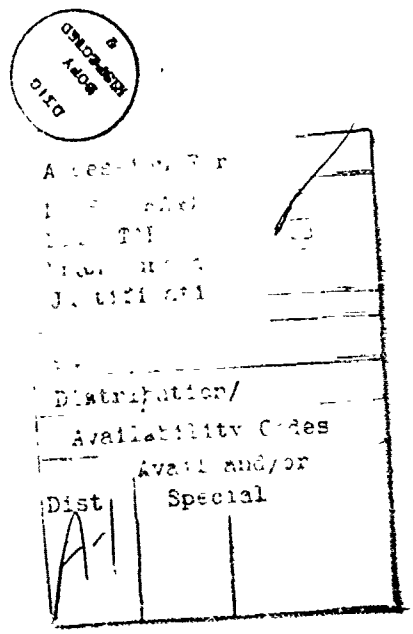
further penetration of agent, but also actually to absorb/extract agent. However, no one single capsule was effective against all chemical agents.



EXECUTIVE SUMMARY

This program has been established to develop and evaluate encapsulated -OCl⁻ materials (bleaches) and chemical warfare agent (CWA) indicators for use as a decon on wounded and incapacitated personnel. An encapsulated decon should help decontaminate CWA exposed personnel and protect attending medical personnel without contaminating either with potentially hazardous decons. Encapsulated indicators would provide positive identification of CWA contaminated sites for treatment or special care.

Development of effective decon microcapsules was based on a series of tasks performed on this study. The preliminary tasks included a literature search and review, polymer-agent absorption/permeation studies, materials compatibility and interaction studies, indicator studies, selection of materials for encapsulation, microencapsulation of -OCl⁻ materials and of indicators, and preliminary evaluations of selected capsules.

This investigation culminated with evaluating selected microcapsules on pig skin samples, with HD, GB, and GD. Results appear encouraging. The best capsule performance observed with HD showed considerable decrease in skin penetration by agent. The best capsule performance observed with GD not only showed no further penetration of agent after capsules were applied, but also appeared to have absorbed a portion of the agent that had already penetrated before capsules were applied.

Dibromo-dimethyl-hydantoin (DBDMH) has been identified and undergone preliminary evaluation as an indicator for HD. Capsules containing $Ca(OCl)_2$ or sodium dichloroisocyanurate dihydrate as core material and chlorinated rubber as capsule wall material were modified by adding a second wall coating of a blend of chlorinated rubber and DBDMH. These capsules provide both a color change and decon function when contacted with HD. Indicator systems investigated for GB and GD are not completely satisfactory although results show some promise.

Leach test results show that some capsules are also resistant to immersion in water for up to 1 hr or more, suggesting that there should be little release of decon material into body fluids in short-term contact. In addition, a brief study showed magnetite can be incorporated into the capsule wall to provide magnetic microcapsules that can be retrieved by a magnet. This capability may provide a method of recovery of capsules after decon activity is completed.

However, further development and optimization work is recommended. While the preceding capabilities have been individually demonstrated by various capsules, the desirable qualities/functions have not yet been combined into a single effective formulation. Incorporation of these into a preferred embodiment of the concept will require further development. Further study is also needed to identify and develop effective indicators for GB and GD and to improve overall decon effectiveness with higher levels of GB/GD destruction. Many results reported are based on a limited number of samples and/or analyses. Replication of such evaluations will be required to provide fully reliable quantitative results and to determine the range of product performance variability.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF TABLES

LIST OF TABLES (Continued)

ENCAPSULATED DECON FOR USE ON MEDICAL PATIENTS

INTRODUCTION

Application of chemical warfare agent decontaminants (DECON) to wounded and/or incapacitated personnel helps to prevent further damage to the patient from the agent; however, many of the more effective DECON materials are strong reactive chemicals that can cause severe tissue damage when applied to skin or open wounds. Encapsulation of DECON with membranes of suitable polymers would solve many problems associated with its use. Capsules designed to release DECON in the presence of organophosphorous or organosulfur compounds when a certain amount of agent has been absorbed would eliminate unnecessary exposure to corrosive, oxidizing DECON for both patients and medical personnel. Incorporating an agent reactive/sensitive dye would aid in the identification of agent contamination and provide for continuous availability of DECON that had not yet been in contact with an agent.

OBJECTIVE

The objective of this program, as stated in RFP F33615-82-K-0612, is the development of a microencapsulated hypochlorite-type chemical warfare agent decontaminant for use on medical patients. The microencapsulated chemical agent decontaminant is to contain an agent reactive/sensitive dye to provide a visual indication of the presence of a chemical agent. Application of the encapsulated DECON to medical patients will help prevent further damage to the patient and provide protection to medical personnel attending to them.

WORK PLAN

The work plan, proposed by Battelle Columbus Laboratories (BCL) in response to the subject RFP, was composed of the following tasks:

Task 1. (RFP Task number 4.1) Literature search. Various literature sources were accessed and reviewed to provide data on $-OCl^-$ source materials, polymer $-OCl^-$ reactions and stability, polymer absorbency for agents, encapsulation of $-OCl^-$ materials (bleaches) and agent sensitive dyes/indicators.

Task 2a. (RFP Task number 4.2.1) Absorbency/permeation study. Investigate at least 12 polymers and "waxes" (potential candidate capsule wall materials) and their interaction with agents GB, GD, and HD.

Task 2b. (RFP Task number 4.2.2) Materials compatibilities studies. Study compatibility and interactions of $-OCl^-$ materials, polymers, solvents, and agent-indicators. Evaluate nonencapsulated $-OCl^-$ materials for effectiveness in deconning GB, GD, and HD.

Milestone A. (RFP Task number 4.3) Based on preceding tasks, select materials for use in subsequent encapsulation studies.

Task 3a. (RFP Task number 4.4) Encapsulation studies. Using the selected $-OCl^-$ materials, polymers, solvents, and indicators, investigate at least two encapsulation processes for development of decon microcapsules.

Task 3b. (RFP Task number 4.4) Capsule evaluation. Evaluate selected microcapsules with GB, GD, and HD directly and with skin tests.

Task 4. (RFP Task number 4.4.1 and 5.1) Final report. Review project results, identify best capsule system(s), and provide recommendations for further development.

SUMMARY

Results appear very promising. Of the more than 40 capsule samples prepared, twelve were evaluated with agent (Tables 18-28). Several show good decon effectiveness (up to 97% with HD, 80% with GB, and 75% with GD). Three capsule samples were evaluated with each agent in pig skin tests. Cadaver skin was not readily available so pig skin was substituted. Previous studies elsewhere have indicated that penetration of a wide number of chemicals through pig skin is similar to penetration through human skin. In this test, agent was placed on a prepared skin sample. Capsules were applied 5 min after agent was added and allowed to remain for 30 min. Capsules and unabsorbed CWA were washed off the surface of each skin sample into a beaker using about 10 ml hexane applied from a wash bottle. This hexane was immediately decanted into a volumetric flask and diluted to 50 ml with more hexane. The skin samples were then processed and analyzed to determine residual (penetrated) agent. Controls with no capsules applied were similarly washed and analyzed. Capsules and hexane wash liquors were also analyzed.

With HD, capsules significantly reduced agent penetration. With GB, one capsule system prevented any further penetration of the skin sample by agent after capsules were added. With GD, capsules appear not only to

prevent further penetration of agent, but also actually to absorb/extract agent already penetrated into skin samples at the time capsules were applied.

Polymers selected for use as capsule wall materials were cellulose acetate butyrate (CAB), chlorinated rubber, polyvinyl butyral, and polyvinylidine copolymer. The $-OCl^-$ materials selected as capsule cores were calcium hypochlorite and sodium dichloroisocyanurate dihydrate. The CAB and chlorinated rubber show greatest promise of the four polymers evaluated. Both $-OCl^-$ materials effectively decon HD, but neither fully decon GB nor GD.

Dibromo-dimethyl-hydantoin was found to be a useful indicator for HD, as well as effective decon (only for HD). In contact with HD, a bright yellow or orange color is formed. Luminol and indole were studied as indicators for GB and GD. These show some promise but will require considerably more development.

Capsules used in tests with agent were also evaluated in a water leaching test. The CAB and polyvinyl butyral, contrary to expectations, performed better than chlorinated rubber or polyvinylidine chloride copolymer. The best samples showed only about 1% of the core material leached after 1 hr in water. The leach test performance may be important to indicate whether capsule core materials will leach in the presence of body fluids.

Two capsule samples incorporated magnetic iron oxide in the capsule wall to demonstrate that magnetic capsules could be prepared. These capsules were successfully sequestered in aqueous dispersion by a small bar magnet. No attempt was made to evaluate removal from whole blood or other body fluids. Further development is needed, but results suggest that magnetic based recovery might be considered for removal of spent capsules from open wounds.

No one single capsule showed best results in all tests. Further work is needed to improve overall performance and bring together into one capsule system the various best performances in the different tests. Further improvement in skin test decon performance is desirable, and can probably be developed. Further development is needed for GB and GD indicators, as well.

RECOMMENDATIONS FOR FUTURE DEVELOPMENT

Results of this feasibility study appear quite promising, but considerable further development will be required to develop a fully functional microencapsulated decon and indicator system which is completely effective against all three CWAs studied (HD, GD, and GB). The ideal microcapsule system is perceived as having these characteristics:

- provides 100% effective decon of HD, GB, and GD absorbed into capsule
- rapidly absorbs agent into capsule wall
- prevents any further agent penetration into skin as soon as capsules are applied to contaminated areas
- extracts/absorbs agent already penetrated into skin
- changes color on contact with agent to provide visual indicator of contaminated sites
- has good storage stability under standard storage conditions
- does not allow release/migration of absorbed agent, decon or other capsule contents out of microcapsules after application to contaminated skin or open wounds
- does not allow leaching of capsule contents by and into contacted body fluids (e.g., blood, perspiration)
- is safe to handle and easy to apply
- is readily removed from skin after agent has been absorbed
- is amenable to safe and easy disposal
- suitable for use in open wounds
- preferably all the preceding characteristics are demonstrated by each and all of the microcapsules in the system.

To develop a product approaching this ideal, several improvements and additional study will be necessary. A follow-on program should include the following tasks:

- identify an indicator or indicator system which is as effective with GB and GD as the DBDMH appears to be with HD.
- develop methods to incorporate these indicators into the microencapsulated decon system and product.
- modify capsule wall composition to further increase absorbence of CWA, minimize agent penetration into skin, and, if possible, extract and absorb agent already penetrated.
- increase decon effectiveness. Several $-OCl^-$ materials show decon effectiveness for HD of 90% to 100% but only up to 70% to 80% for

GB and GD. A formulated capsule core composed of a mixture of decons may be necessary to provide thorough decontamination of GB, GD, and HD by each microcapsule. A composite core in all capsules is probably more desirable than a blend of capsules, since the latter would probably not completely decon contaminated skin. Another option to be studied is to incorporate one decon in the capsule wall and others in the capsule core, especially if materials are incompatible in processing, storage or application/use. Composite cores may be prepared by blending and agglomeration fine powders, prepared from hot melt, by prilling, or formed in layers by application of encapsulation processes.

- investigate other capsule wall materials to increase CWA absorbence. This effort should include additional polymers, blends of polymers, addition of plasticizers and/or absorbent inorganic materials which themselves do not form good capsule walls. Such materials may be incorporated into the capsule wall during encapsulation or be applied as a separate surface layer after encapsulation.

- incorporate magnetic materials, such as magnetite, in capsule wall and/or capsule core to provide magnetic capsules. Such capsules should be easier to locate and remove/recover from open wounds and body fluids. This magnetic material must be selected and incorporated in ways that do not reduce capsule absorbency, decon effectiveness, indicator effectiveness, or storage stability.

- incorporate materials and processes providing best performances in preceding functions into a single microcapsule system.

- increase and extend evaluations. Key evaluations, such as pig skin tests, should be run in, at least, triplicate. This should be followed by human cadaver skin tests and then by testing with suitable animal models such as pigs or perhaps athymic ("nude") mice with human skin grafts. Storage stability of capsules should be determined, quantitatively, under a variety of selected conditions.

A study based on these recommendations should lead to the development of an improved encapsulated decon which will more nearly approximate the ideal product described earlier in this section. Promising results of the current study are interpreted as indicating a good probability of developing a successful product.

EXPERIMENTAL DETAILS

The following sections describe details of the experimental work done on this project.

Task 1. Literature Search and Review

With respect to $-OCl^-$ encapsulation and handling procedures, existing BCL files were reviewed, and a computer search was made of Chemical Abstracts Index (1972-81), NTIS (1964-82), Engineering Index (1970-82), and the U.S. Patent Index (1976-82). The literature search provided 65 references, about half of which appeared to be relevant (at least marginally) to encapsulation and/or handling of $-OCl^-$ materials. Copies of relevant references, articles, and patents were obtained and reviewed.

The patent literature examined provided relatively little data directly and immediately relevant to this study. However, Reference List A in Appendix A is a listing of patents with some limited relevance to this study. References A-1 through A-17 and A-20 relate to coating materials and processes for encapsulation of bleach particles. The function of these coatings is to provide delayed release of bleach in aqueous media and/or provide longer stability of component materials in detergent formulations. Reference A-15 (U.S. Pat. No. 3,647,523) provides a brief list of chlorinated solvents suitable for use in processing $-OCl^-$ materials.

Most references to coatings for the bleach materials relate to fatty acids, fatty acid esters, alcohols, glycols and paraffin waxes as the coating material although polystyrene and styrene acrylic copolymers are also mentioned. However, since these coated $-OCl^-$ materials are intended for use as laundry and dishwashing detergent additives, the functions of the capsule wall, and hence the wall composition, are quite different from capsule walls developed for this study.

Many of the patents involve inorganic coatings or one class of organic coatings; long chain fatty acids (such as stearic acid). Some variations involve an initial coating (capsule wall) of fatty acid followed by a second coating of other materials, such as sodium stearate. The selected fatty acids are waxy solids at ambient temperatures. They are sprayed as a hot melt onto particles of selected $-OCl^-$ materials such as potassium dichloroisocyanurate. Various processing systems may be used, but major emphasis is on fluidized bed coating (encapsulation) processes. Coated particles described are generally 1-2 mm, which is larger than the preferred size(s) for this project. The coated particles are claimed to remain stable for extended periods of storage, to release $-OCl^-$ (as a bleach) in hot/warm water and to prevent "pinholing" (damage to fabrics caused by solid bleach particles in direct contact).

However, release of the $-OCl^-$ (bleach) decreases with thicker coatings of fatty acids and with the use of relatively high-melting fatty acids.

Reference A-18 ("Method of Coating Chloramine and Product Thereof") describes coating of chloramine with sodium stearate, using a chloroform solution and pan coating techniques. Reference A-19 describes the coating of soda lime particles with sodium permanganate and as being "useful for the absorption of certain gases used in warfare and encountered in the industries, such as arsine, phosgene and other chlorinated organic compounds."

Patent Reference List B (Appendix) is a listing of patents that were reviewed but judged to have very little or no relevance to this current study. However, some materials and processes, relating to increasing the stability and shelf-life of $-OCl^-$ materials, are described. These may be more relevant to a more-detailed Phase II, follow-on study of encapsulated $-OCl^-$ decon.

Only a limited amount of literature that discusses indicators for agents was found and reviewed. These are (1) "Military Chemistry and Chemical Agents" TM3-215/AFM 355-7, Department of the Army and the Air Force (December 1963), and (2) "Government Report Literature Survey on the Detection of Selected CW Agents", by R. E. Wyant (of Battelle) to Naval EOD Facility (February 5, 1979). Three additional references are cited in footnotes on pages 52 and 54.

Information on the interactions between polymeric materials and chemical warfare agents was reviewed, especially with respect to chemical warfare agent/polymer absorption and permeation. The prior work has been concerned mainly with absorption of agent as measured by weight change and change in physical properties of exposed polymers. Sources for this information were primarily compilations of previous work carried out at the U.S. Army's Chemical Systems Laboratory (Aberdeen Proving Ground, Maryland) and some recent work at Battelle's Hazardous Materials Laboratory (HML). Literature covering polymer solubility parameter data was also reviewed. Available information on (1) sorption and solubility properties of polymers with $-OCl^-$ and solvents and (2) conditions required for forming films of the polymers were considered in final selection of polymers for evaluation in Task 2a.

To establish handling and evaluation procedures for compatibility studies of $-OCl^-$ materials with solvents, previous proprietary work at Battelle Columbus Laboratories on encapsulation of bleaches was also reviewed. Relevant procedures were adapted for use in this program.

Some additional literature was identified and reviewed during the course of work on Tasks 2 through 4. These references are cited in the appropriate parts of following sections of this report.

Task 2a. Polymer-CWA Compatibility Studies

Polymer film compatibility with HD, GB, and GD was studied through three comparative evaluations: (1) film permeability to CWA, (2) solubility parameter and hydrogen bonding indexes of polymers compared to similar data for CWA, and (3) CWA vapor sorption into selected polymer films.

Permeability of Coating Films to Chemical Agents--Ten coating resins were identified (from past work) as being sorptive to agents and have been screened for stability to the candidate decons. Films of these resin materials (approximately 25 μm thick) were prepared by casting on glass from solvent solutions. Solvent-cast films were used because they more nearly simulate coatings formed by the microencapsulation processes which were used later in this project. Most films were separated from the glass (as free films) rather easily. Three materials (Saran®, Elvax®, and Viton®) were separated more easily if placed in a freezer for a short period of time, prior to the attempted separations.

The initial screening tests were run in a permeation cell on which the film (about 30 cm^2 circle) was supported by a stainless steel frit and chemical agent drops were placed on the surface of the film. It was found that many of the films softened and threatened to contaminate the frits.

Because of these problems, the screening study was continued by placing smaller portions of film (about 4-5 cm^2) on white paper. A 1 μℓ drop of agent was then put on the film and observed through a magnifying lens. The tests with HD were conducted in this manner and when the HD permeated the film a "wet" spot appeared on the paper. However, when the films were lifted a "hole" was observed in some films and softened resin was attached to the paper.

For the GD and GB agents two samples of film were then evaluated, one in contact with the paper, and one suspended over the paper. This modified procedure was used to determine if the films were soluble in the agents and a hole was formed spontaneously, or if the hole was caused by manual removal of the film (adhesion of the softened film to the paper).

As can be seen from the data presented in Table 1, seven of the films were permeated by the HD in less than 30 min. GD and GB are more volatile so permeation and evaporation were competing processes. In a number of cases the film was softened and the drop appeared to persist. Probing the apparent drop, however, showed it to be a swollen or softened area of the film. Only one film appeared to form a hole on contact with the agents. This film was based on Viton® and the agent was GB. Some films, such as polycarbonate, polystyrene, and polycaprolactone, appeared to be "wet" by

the agent with the droplet spreading out. This spreading either diluted the softening effect or speeded evaporation of the agent (or both). Data showing these results with the GB and GD agents and the candidate films are also presented in Table 1.

Two other materials had been considered as capsule wall candidates. These are polyethylene and stearic acid. However, they are not included in these tests become of potential problems in film preparation and encapsulation processes. Polyethylene is only very slightly soluble in a few hot solvents, such as xylene or trichloroethylene. In past work at Battelle, solid particles of inert materials have been dispersed in a heated xylene solution of polyethylene, and coated by cooling the solution under controlled conditions. However, adding particles of strong oxidizers, such as the $-OCl^-$ materials of interest here, was deemed too hazardous for further consideration.

The stearic acid was studied in the compatibility studies described later in this report, but this material is quite brittle and not easily handled as a thin film. Consequently, it too was dropped from further evaluations.

Solubility Parameters--The literature was examined for solubility parameters for the polymers used in this study. Table 2a lists the solubility parameter ranges found. No data was found for polycaprolactone PCL700 or for Viton® B. Solubility parameters and hydrogen bonding index for solvents and agents used in this study are shown in Table 2b.

Comparison of solubility parameters and hydrogen bonding indexes for polymers (Table 2a) with that for CWA (Table 2b) indicates that the cellulose acetate butyrate and polyvinylidine chloride copolymers should be sorptive of and/or permeable to HD. Polystyrene, polycarbonate, and chlorinated rubber are also possible candidates (i.e., based on the 10.6 solubility parameter of HD and 2.7 hydrogen bonding index falling within the solubility parameter range of the polymer as shown in the "weakly" column of Table 2a). A similar comparison for GB and GD suggests chlorinated rubber, polyvinyl butyral, and cellulose acetate butyrate are likely to be sorptive of and/or permeable to the GB and GD agents.

Film: Agent Absorption-Desorption Studies--Technical problems were encountered in using a Cahn Electrobalance to screen the CWA absorption/desorption properties of the candidate polymeric capsule wall materials. The Cahn Electrobalance procedure involves exposing a polymer sample to CWA vapor and measuring the weight of the sample again as a function of time. Efforts were unsuccessful in generating a constant CWA vapor "challenge" concentration over the absorption time period (several hours).

TABLE 1. SCREENING TESTS FOR PERMEABILITY OF FILMS BY CHEMICAL AGENTS[a]

Film Material	Observation		
	Agent HD	Agent GD	Agent GB
CAB Cellulose acetate butyrate	Wet paper in about 7 min	Softened spot on film, no hole	Softened spot on film, no hole
Lexon® Polycarbonate	Wet paper in about 1 min.	Appeared to wet film and spread, apparently evaporated as film appeared unchanged	Appeared to wet film and spread, no change in film
Styron® Polystyrene	Wet paper in about 2 min	Same as Lexan but slightly less spread	Same as Lexan, less spread and spot was visible, slight softening
Butvar® B-76 Polyvinyl butyral	Wet paper in about 10 min	Same as CAB, softened film	Softened film same as CAB
Butvar® B-73 Polyvinyl butyral	No apparent change after 30 min	Same as CAB	Same as CAB
Parlon® Chlorinated rubber	Wet paper in about 2 min	Wet paper in about 20 min	Wet paper in about 15 min
PCL Polycaprolactone	Wet paper in about 5 min	Same as Lexan, less spread	Same as Lexan, less spread
Saran® Polyvinylidene chloride	Wet paper in about 0.5 min, hole	Wet paper in about 5 min	Wet paper in about 5 min and formed hole in suspended film
Elvax® Ethylene vinyl acetate	No apparent change after 30 min	Swelled and wrinkled	Swelled and wrinkled
Viton® Polyester	No apparent change after 30 min	Swelled and wrinkled, wet paper in about 9 min	Wet paper in about 5 min, dissolved suspended film leaving hole

[a] Performance of solvent cast films may differ greatly from blown or hot melt extruded films. Often the grade or specific solution polymer chosen may differ in average molecular weight or other significant parameters from the extrusion grades.

TABLE 2a. PUBLISHED SOLUBILITY PARAMETER INFORMATION FOR POLYMERS

Polymer Name	Hydrogen Bonded Solvents[a]		
	Weakly	Moderately	Strongly
Ethylene Vinyl Acetate (Elvax® 210)	7.3-9.8	0	0
Polystyrene (Styrene® 6664)	8.5-10.6	9.3	0
Polycarbonate (Lexan®)	9.5-10.6	9.3-9.9	0
Chlorinated Rubber (Parlon® S125)	8.5-10.6	7.8-10.8	0
Polyvinylidine Chloride Copolymer (Saran® F220/F310)	9.5-11.1	10.8-14.7	0
Polyvinyl Butyral (Butvar® B76)	9.0-9.8	8.4-12.9	9.7-12.9
Cellulose Acetate Butyrate (CAB 381-20)	11.1-12.7[b]	8.5-14.7	12.7-14.5
Polyvinyl Butyral (Butvar® B73)	0	9.9-12.9	9.7-14.3

[a] Weakly hydrogen bonded implies a hydrogen bonding index around 2.5, moderately bonded is about 5.5, and strongly bonded is about 8.5.

[b] Battelle's experience with CAB 381-20 indicates that this should be 9.3 to 12.7. For example, CH_2Cl_2 and $CHCl_3$ are solvents.

TABLE 2b. SOLUBILITY PARAMETER INFORMATION ON SOLVENTS AND AGENTS

Solvent/Agent	Solubility Parameter	Hydrogen Bonding Index [a]
Freon® TF	7.2	2.5
n-Hexane	7.3	2.0
Cyclohexane	8.2	2.2
Toluene	8.9	3.3
Dichloromethane	9.7	2.5
Ethyl acetate	9.1	5.2
Methyl ethyl ketone	9.3	5.4
Acetone	10.0	5.9
Ethanol	12.7	8.5
GB	9.0(9.10) [b]	5.4
GD	(8.41) [b]	c
HD	10.6	2.7

[a] According to DuPont system.

[b] The values in parentheses are calculated values. Others are experimentally determined values.

[c] Believed to be about 5.5.

In general, solubility and diffusivity of an organic penetrant (CWA) in a polymer are dependent on the concentration of the penetrant in the polymer. This penetrant concentration in the polymer is, in turn, dependent on the challenge concentration. Therefore, interpretation of absorption data obtained with a varying challenge concentration is difficult and can be misleading. This difficulty is particularly pronounced when comparing the organic liquid absorbing properties of several polymers which is the main objective of the CWA/polymer absorption studies in this program.

For these reasons, liquid CWA absorption/desorption experiments were proposed and attempted instead of the Cahn Electrobalance vapor absorption studies. Since the encapsulated decontaminants are being developed to absorb liquid CWA, these liquid absorption/desorption experiments should provide more valid "real world" results.

The following liquid CWA absorption/desorption procedures have been successfully used in other research programs and were proposed for use in this program:

(1) Test slabs (2.5 cm by 2.5 cm) are cut from each polymer sample.

(2) An automatic pipette is used to contaminate each of several (up to six) preweighed test slabs of a single polymer with 10 μl of CWA. The CWA is placed in strips near the center of each sample and covered by a watch glass immediately after placement to reduce evaporation losses.

(3) At selected intervals after CWA placement, the liquid CWA remaining on the surface of a test sample is blotted using filter paper and the sample is weighed to obtain the amount of absorbed CWA. The amount of unabsorbed CWA is determined by extracting the filter paper with chloroform and analyzing the extract by gas chromatography. The time periods between weighings are a function of the amount of CWA absorbed by the first sample weighed. The first sample is generally weighed about 5 min after contamination. Also, after weighing, a test sample is extracted with chloroform, and the extract is analyzed for CWA using gas chromatography. The extraction supplements the absorption results obtained by weighing.

At the time the last sample is weighed in an absorption run, a contaminated sample is prepared for desorption measurements. The CWA/polymer

contact time for the desorption sample corresponds to the contact time of the last absorption sample. The following procedures are then used for desorption determinations:

(1) Unabsorbed CWA is removed using filter paper, and the test sample is placed in a desorption test chamber. A 1 liter/min air stream is passed through the chamber for a period of time (up to 170 min), and desorbed CWA is trapped for gas chromatographic analysis using chloroform bubblers. Several bubbler samples are taken at selected time intervals beginning with the initiation of air flow.

(2) After the desorption test period, the test slab is extracted with chloroform to determine the amount of CWA remaining in the polymer. Also, the filter paper used in removing unabsorbed CWA is extracted with chloroform. The test slab and filter paper extract are analyzed for CWA using gas chromatography.

Attempts were made to measure the sorption of liquid HD, GD, and GB by films of the candidate polymeric capsule wall materials, following the experimental procedure outlined above. Difficulties were encountered when it was found that, in some instances, the liquid CWA softened and solubilized the film samples of the candidate polymers. For polymer samples which became tacky and/or lost mechanical integrity, it was not possible to blot off only the unabsorbed CWA prior to making weight gain measurements.

As a result, laboratory efforts were again directed toward CWA vapor sorption. Vapor sorption provides the same information as liquid sorption in regard to relative CWA affinity of the polymer candidates but does not require the removal of standing (unabsorbed) liquid CWA prior to weight measurements.

The same general procedure was employed for CWA vapor sorption measurements as proposed for liquid sorption measurements with the exception that the film samples were exposed to CWA vapor and not to CWA liquid. Vapor exposure was accomplished by placing each film sample of a polymer candidate on a watch glass which was then placed in a closed container containing CWA vapor at saturation level. The CWA vapor was generated by a wick (absorbent paper) which contained approximately 100 µl of sorbed CWA. Since the film samples were separated from the wick by a watch glass, they did not contact liquid CWA. Each film sample was one square inch in size. Exposure times evaluated varied according to type of polymer and CWA. Test temperatures were all 21.0° to 21.7° C.

Samples of each candidate polymer were removed after selected exposure times and were weighed to determine the amount of sorbed CWA. To

eliminate the potential problem of disturbing the CWA vapor concentration each time a film sample was removed for weighing, each film sample was contained in a separate CWA vapor atmosphere (closed container). This exposure to CWA and weighing steps were repeated with separate film samples for several exposure times.

The Cahn Electrobalance, however, could not be used for vapor sorption measurements under the condition of stagnant (not flowing) saturated CWA vapor. Such measurements would expose the balance mechanism of the Cahn to the potentially corrosive CWA vapor. Consequently a suitable laboratory balance was used for obtaining sample film weights before and after CWA absorption.

Based on these measured weight changes, sorption data were calculated as a percent weight increase and plotted as a function of time (see Table 2c and Figures 1, 2, and 3). As shown in the graphs, the CAB and Parlon® S125 were more absorbent than the Butvar® B73 and Saran® F310, especially with HD and GD. For GB, the Parlon® S125 absorption results are closer to Butvar® B73 than to the CAB. This data agrees well with capsule test results which also show that CAB and Parlon® S125 generally provided faster and more complete sorption of agent than Saran® F310 and Butvar® B73. This data is also consistent with the solubility parameters and hydrogen bonding index data presented earlier in this report.

Task 2b. Decon Compatibility Studies

Compatibility and reactions between the $-OCl^-$ decon materials and selected solvents, polymer solutions, and CWA were studied. Efforts and results are discussed in the following sections of this report.

Solvent $-OCl^-$ Compatibility--A procedure was established for determining the compatibility of candidate $-OCl^-$ materials with selected solvents, such as those commonly used in various encapsulation processes. The procedure used was:

- place 0.5 g of $-OCl^-$ material in a small vial (fitted loosely with polyethylene cap, modified to allow insertion of thermocouple)
- add 4 ml of selected solvent and immediately cap and insert thermocouple
- note temperature change, gas evolution, color change, and dissolution for several minutes

TABLE 2c. WEIGHT CHANGE OF POLYMER FILM SAMPLES EXPOSED TO CWA VAPOR

Polymer [a]	CWA	% Weight Changes After Various Exposure Times Shown (min)											
		10	15	20	25	30	35	40	45	60	90	120	180
CAB 381-20	GB	--	1.69	--	2.02	--	2.58	--	--	4.20	5.02	--	--
	GD	--	0.14	--	--	0.07	--	--	1.05	1.02	--	--	--
	HD	--	--	--	--	0.28	--	--	--	0.51	1.02	0.74	2.05
Parlon	GB	0.51	--	--	--	0.24	--	--	--	0.58	0.74	--	--
	GD	--	-0.29	--	--	0.31	--	--	-0.07	0.00	--	--	--
	HD	--	--	--	--	-0.06	--	--	--	0.24	1.66	1.95	1.07
Saran F310	GB	0.41	--	0.14	--	--	--	-0.08	--	-0.08	--	--	--
	GD	--	-0.35	--	--	0.31	--	--	0.08	-0.14	--	--	--
	HD	--	--	--	--	0.00	--	--	--	-0.51	-0.23	0.16	-0.16
Butvar B73	GB	0.07	--	0.44	--	--	--	-0.07	--	0.20	--	--	--
	GD	--	0.47	--	--	0.23	--	--	0.85	0.13	--	--	--
	HD	--	--	--	--	0.33	--	--	--	0.23	0.32	0.82	1.20[b]

[a] Polymer film samples were about 1 in^2

[b] Sample erroneously weighed after 165 min rather than 180 min.

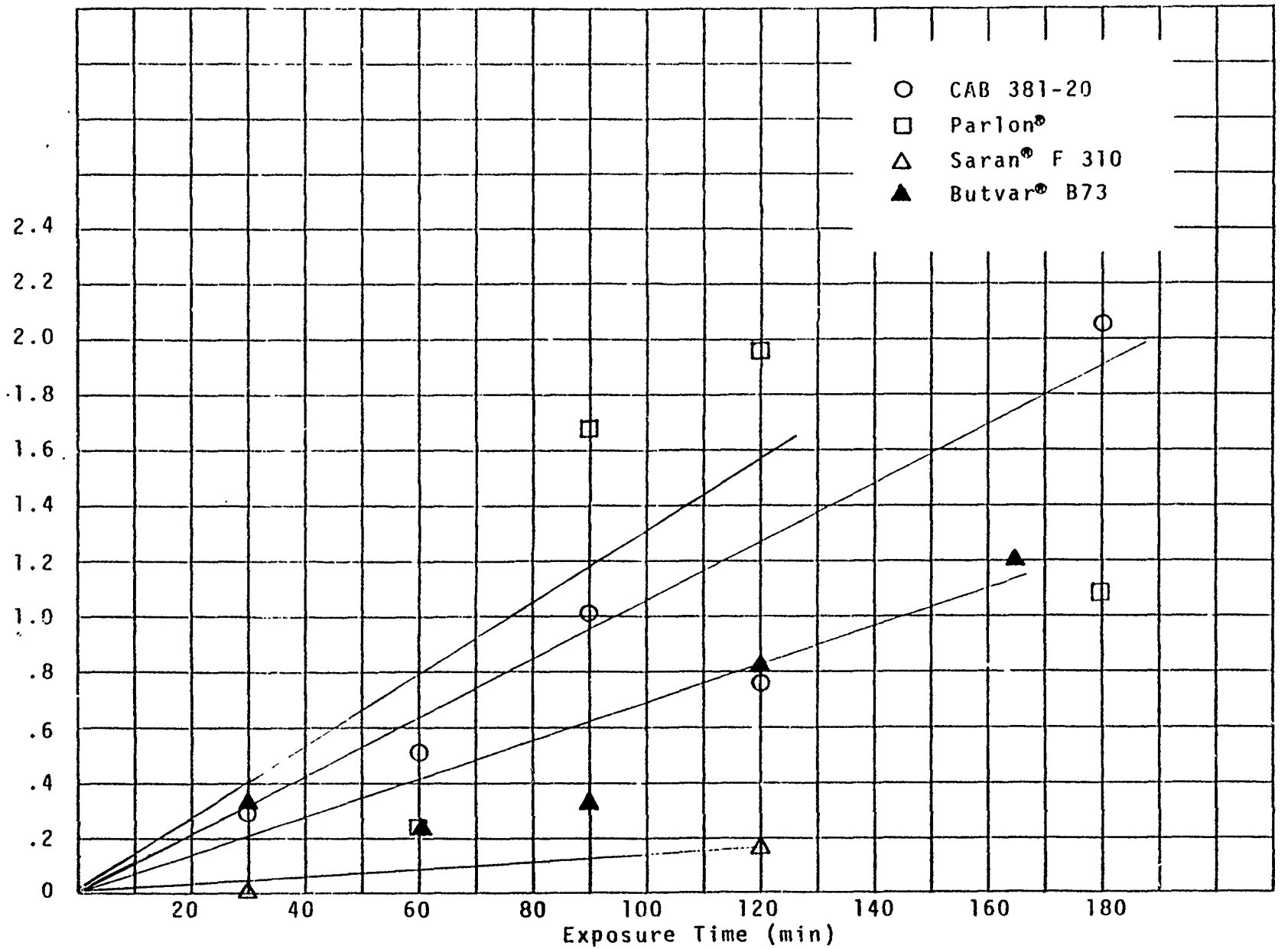


Figure 1. Absorbence of HD by polymer films.

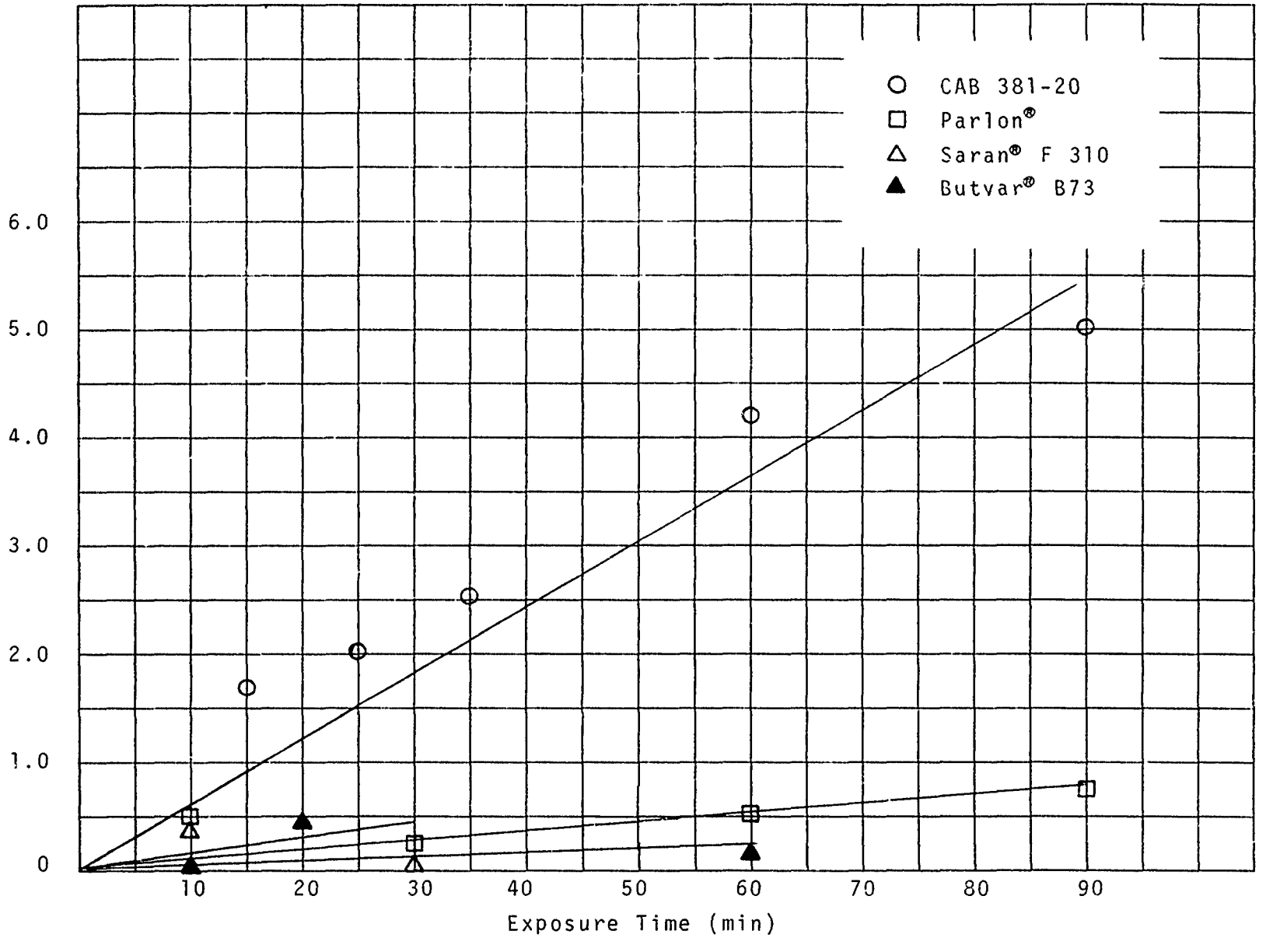


Figure 2. Absorbence of GB by polymer films.

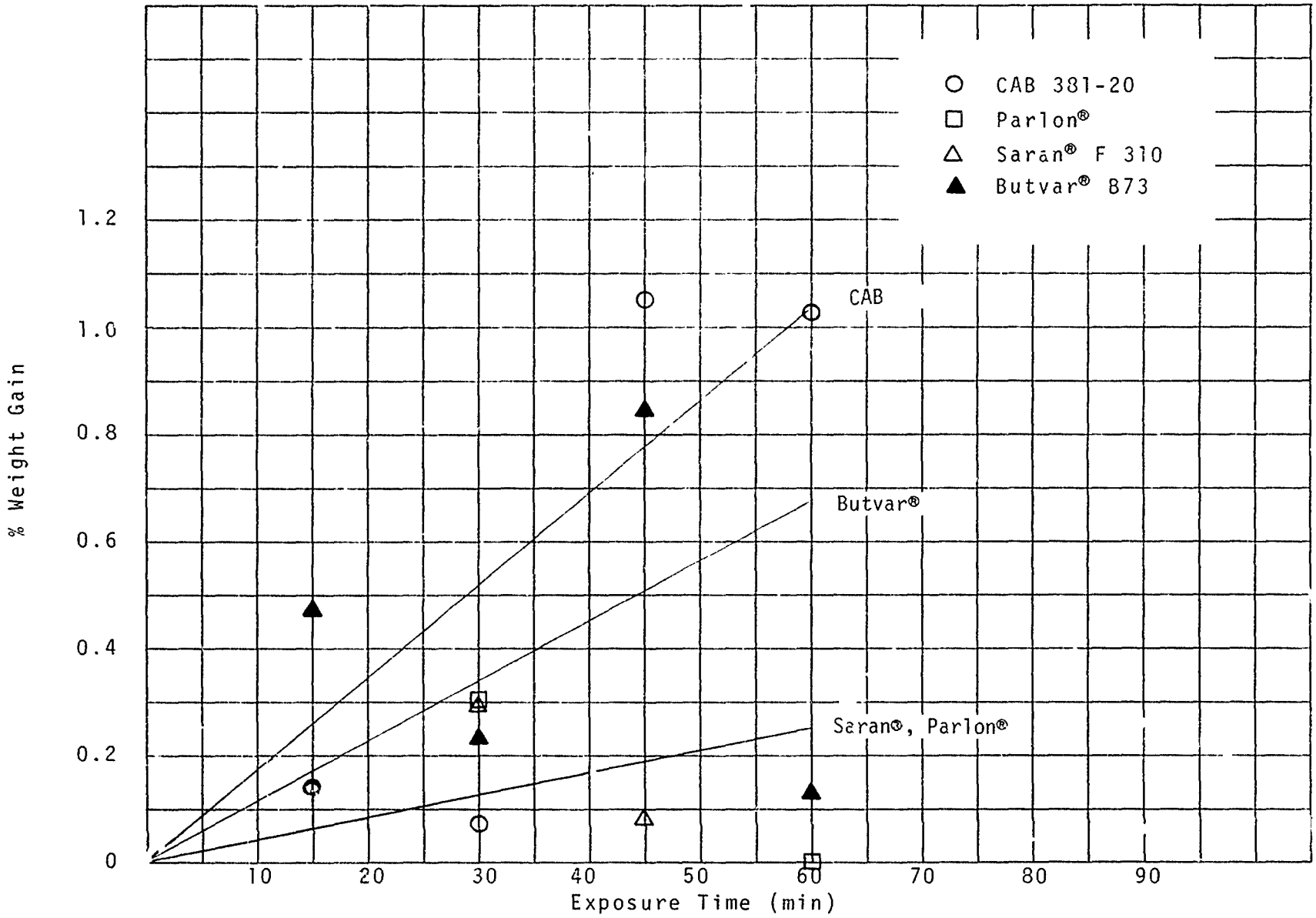


Figure 3. Absorbence of GD by polymer films.

- remove thermocouple and special cap
- secure with standard friction-fit cap and allow to stand for 18 hr
- note changes in $-OCl^-$ material and solvent.

Ten different "bleaches" ($-OCl^-$ materials) were evaluated for compatibility with 9 different "solvents." These solvents were selected from among a list of organic fluids commonly used in encapsulation processes. Resulting data are shown in Table 3 and provide a 90 point matrix of bleach-solvent compatibility evaluations. Only two combinations showed temperature increases: lithium hypochlorite with acetone or with methyl ethyl ketone. Several bleaches showed no reactions in any of the solvents tested. Cyclohexane showed no reaction with any of the bleaches tested.

This study did not, by itself, eliminate any of the bleaches from further consideration. The study, however, identified some combinations to be avoided. Actual selection of candidates for Task 3 (encapsulation studies) was made after the bleach-agent (CWA) reaction studies were completed.

Bleach-Polymer Solution Compatibility Studies--Another series of tests were run to investigate the compatibility of the candidate bleach materials with solvent solutions of ten different polymers and stearic acid. This test was similar to the one for solvents, except 5% polymer solutions (mostly in CH_2Cl_2) were used with the bleaches instead of the solvents alone. Saran® F 310 was dissolved in methyl ethyl ketone (MEK) because it is the best conventional solvent for that polymer. Ethyl acetate is the preferred solvent for Viton® B and was used in these tests.

Polymers were selected for this test based mostly on two factors: (1) past effectiveness as encapsulating materials, and (2) absorbency for one or more chemical agents (as indicated by available literature). Table 4 summarizes observations from this compatibility study. Nearly half of the data points in the table matrix are nro (no reaction observed). Comparison of the data presented in these tables with results from the studies of the interactions of bleaches with CWA and of permeability of selected polymer films to CWA helped provide the basis for selecting candidates for the encapsulation studies. The BCL study of CWA absorption (reported under Task 2a) was not used as a basis for polymer selection because of difficulties and delays in generating the data. This absorption study data was not available until later in the project and hence was used as a supplement.

Decon-CWA (HD) Reactions--The ten candidate decon materials were screened for efficiency in reacting with HD under relatively dry conditions. A solid powdered decon material currently in use, STB, was

TABLE 3. SUMMARY OF BLEACH-SOLVENT COMPATIBILITY

-OCl- Material	Time [a]	Acetone	Ethyl acetate	Dichloro-methane	Toluene	Cyclo-hexane	Hexane	Petroleum ether	Methyl ethyl ketone	Freon® TF
Sodium dichloroisocyanurate dihydrate (ACL 56)	a	nro [b]	nro	nro	nro	nro	nro	nro	nro	nro
	b	"	"	"	"	"	"	"	"	"
Potassium dichloroisocyanurate (ACL 59)	a	"	"	"	"	"	"	"	"	"
	b	"	"	"	"	"	"	"	"	"
Sodium dichloroisocyanurate (ACL 60)	a	"	"	"	"	"	"	"	"	"
	b	"	"	"	"	"	"	"	"	"
Lithium hypochlorite	a	82→130°F [c]	"	"	"	"	"	"	81→146°F [c]	"
	b	res. formed	"	"	"	"	"	"	res. formed	"
Calcium hypochlorite	a	nro	"	"	"	"	"	"	nro	"
	b	"	"	"	"	"	"	"	"	"
Chlorinated trisodium phosphate	a	"	"	"	"	"	"	"	"	"
	b	"	"	"	"	"	v.sl. yellow	"	"	"
Dichloro dimethyl hydantoin	a	PS	PS	PS, cooled [d]	"	"	nro	"	PS	"
	b	PS	PS	PS	"	"	v.sl. yellow	"	needles ppt.	"
Bromochloro dimethyl hydantoin	a	Sol., yellow	nro	Sol., cooled [d]	"	"	nro	"	Sol., yellow	"
	b	" "	PS, yellow	Sol., yellow	yellow	"	v.sl. yellow	"	" "	orange
Dibromo dimethyl hydantoin	a	Sol., yellow	sl. yellow	v.sl. yellow	nro	"	nro	"	Sol., yellow	nro
	b	" "	yellow	yellow	yellow	"	v.sl. yellow	v.sl. yellow	" "	orange
N-chlorosuccinimide	a	PS, cooled [d]	nro	PS, cooled [d]	nro	"	nro	nro	PS, cooled	nro
	b	Sol.	PS	PS	"	"	"	"	PS	"

[a] a = 3-5 minutes after solvent added; b = 18 hr after solvent added.
[b] nro = no reaction observed, res. = residue, PS = partially soluble, sol. = soluble, v. = very, sl. = slightly, ppt. = precipitated.
[c] Lithium hypochlorite/acetone heated rapidly, but lithium hypochlorite/MEK heated very little for nearly 5 min, then heated rapidly
[d] Apparently a negative heat of solution (4 to 8°F cooling observed).

TABLE 4 SUMMARY OF BLEACH/POLYMER-SOLUTION COMPATIBILITY [a]

-OCl- Material	Time [b]	CAB 381-20 cellulose acetate butyrate	Elvax® 210 ethylene vinyl acetate	Lexan® poly-carbonate	Butvar® B73 polyvinyl butyral	Butvar® B76 polyvinyl butyral	Styron® 6664 polystyrene	Parlon® S125 chlorinated rubber	PCL 700 polycapro-lactone	Saran® F220 vinylidine chloride copolymer	Viton® B	Stearic [c] acid
Sodium dichloroisocyanurate dihydrate (ACL 56)	a	nro [d]	nro	nro	nro	nro	nro	nro	nro	nro	nro	nro
	b	"	"	pink	"	yellow	"	"	"	"	"	"
Potassium dichloroisocyanurate (ACL 59)	a	"	"	nro	"	nro	"	"	"	"	"	"
	b	"	"	v.sl pink	v sl yellow	v sl yellow	"	"	"	"	"	"
Sodium dichloroisocyanurate (ACL 60)	a	"	"	nro	nro	nro	"	"	"	"	"	"
	b	"	"	pink	v sl yellow	yellow	"	"	"	"	"	"
Lithium hypochlorite	a	"	"	nro	nro	nro	"	"	"	76-161°F	"	79+85°F
	b	"	"	v sl. yellow	"	"	"	"	"	orange, ppt.	"	gelled
Calcium hypochlorite	a	"	"	nro	"	"	"	"	"	nro	"	80+72°F
	b	"	"	yellow	v.sl. yellow	v.sl yellow	"	"	"	"	"	gelled
Chlorinated trisodium phosphate	a	"	"	nro	nro	nro	"	"	"	"	"	gelled
	b	"	"	v.sl. yellow	"	"	"	"	"	"	"	gelled
Dichloro dimethyl hydantoin	a	80+71°F	80+71°F	76+65°F	75+70°F	75+70°F	76+68°F	75+69°F	75+68°F	PS	PS	80+70°F
	b	PS	PS	PS, sl. yellow	PS, yellow	PS, yellow	PS	PS	PS	PS	P"	sl. residue
Bromochloro dimethyl hydantoin	a	80+75°F	79+73°F	76+69°F	75-104°F	76+100°F	75+71°F	75+71°F	v.sl. yellow	PS	sl yellow	80+74°F
	b	PS, yellow	PS, yellow	PS, yellow	v. red	v. red	PS, yellow	orange	orange	yellow	yellow	PS, orange
Dibromo dimethyl hydantoin	a	nro	nro	sl yellow	76 102°F	75 104°F	sl yellow	nro	nro	sl. yellow	sl yellow	PS, yellow
	b	yellow	sl. yellow	yellow	v red	v. red	orange	orange	orange	PS, orange	yellow	PS, orange
N-chlorosuccinimide	a	79+73°F	80+73°F	78+73°F	78+73°F	79+75°F	79+75°F	77+72°F	79+73°F	77+75°F	nro	79+73°F
	b	PS	PS	sl. sol	PS, gel.res.	PS	PS	PS	PS	PS	PS	PS

[a] All solutions 5% polymer in solvent All dichloromethane solvent except Saran and Viton
[b] a = 5-10 minutes, b = 18 hours after polymer/solvent added to -OCl- material
[c] Stearic acid is not a polymer, but is included as a candidate encapsulant
[d] nro = no reaction observed.

included in the screening evaluations. For screening purposes, the HD was exposed to about 20 times as much decon material (on a molar basis). The solid decon materials were weighed into small centrifuge tubes and 1 μl (1.27 mg) of HD was placed on the solid particles. Care was taken to avoid getting any of the agent on the tube walls so that as much as possible would be available for reaction. After selected exposure times (described below) chloroform was added to the tube and the contents mixed thoroughly. The mixture was then centrifuged and the liquid portion was sampled for analysis by gas chromatography. Any changes in the liquid or solid residue were noted.

The results of the screening tests are presented in Table 5. It was thought that the reaction of agent with solid decon materials might be slow, so the materials were first exposed for 60 min. Since all of the materials reacted (all but two almost completely), a 5-min exposure time was used for the second screening. The results of the shorter exposure were essentially the same as for the 1-hr exposures, except for the chlorinated trisodium phosphate. Substantial amounts of HD were found after reaction with potassium dichloroisocyanurate and chlorinated trisodium phosphate at both 5-min and 1-hr exposures. The small amounts of HD (less than 6%) found in three samples may result from problems in handling the small quantities of reactants. Conversely, calcium hypochlorite and lithium hypochlorite exhibited extreme reactivity with HD.

The dibromo- and bromochloro-substituted hydantoins gave an intense red-orange color in contact with HD. This intense color may serve as an indicator for presence of agent. However, it apparently is nonspecific, in that at least some coloration was observed in some mixtures of these materials and solvents as presented earlier in this report.

Decon-CWA (GD and GB) Reactions--The candidate decon materials were screened for effectiveness in reacting with GD and GB under relatively dry conditions. The procedure followed was the same as for HD. The screening tests were run first for 5 min, and then selected materials were again checked after a 60-min exposure. The results of the screening tests with GD are shown in Table 6.

The 5-min exposure tests with GD showed sodium dichloroisocyanurate dihydrate to be singularly highly effective. Calcium hypochlorite and STB also had significant decon action on GD. However, the 60-min exposure did not confirm the effectiveness of the sodium dichloroisocyanurate dihydrate that was observed in the 5-min test. Using the same test procedure with GB, unexpected low results were observed even with the control.

These tests must be considered only as screening evaluations since only 20-40 mg of solid decon candidate were treated with 1 μl (about 1 mg) of liquid agent. Also, in this test procedure, the HD appeared to be more reactive than the G-agents. This judgment is based on observations of the

TABLE 5. REACTIVITY OF CANDIDATE DECON MATERIALS WITH HD

Materials	Molecular Weight	60-Min Exposure		5-Min Exposure		Remarks
		Milligrams	Unreacted HD, Micrograms	Milligrams	Unreacted HD, Micrograms	
Control (HD only)	159	1.27	1135	1.27	1085	--
Sodium dichloroisocyanurate, dihydrate	256	40.2	0	41.2	0	--
Potassium dichloroisocyanurate	236	37.7	492	40.6	527	--
Sodium dichloroisocyanurate	220	37.9	0	37.5	0	--
1,3-Dibromo-5,5-dimethyl hydantoin	286	46.6	0	45.6	64	Red-orange spot on solids. Solids dissolved in $CHCl_3$ with red-orange colored solution.
1,3-Dichloro-5,5-dimethyl hydantoin	197	41.1	0	36.6	0	Yellow spot on solids. Solids dissolved in $CHCl_3$.
Bromochloro-5,5-dimethyl hydantoin	241	41.0	0	39.9	0	Orange spot on solids. Solids dissolved in $CHCl_3$ with orange colored solution.
STB (Super Tropical Bleach)	256	45.7	0	42.1	0	--
Chlorinated trisodium phosphate	882	142.5	721	139.7	1118	--
Calcium hypochlorite	215	36.4	0	38.2	0	Reacted violently as soon as contacted. Residue appeared scorched.
Lithium hypochlorite	58	13.2	49	10.6	0	Reacted with evolution of gas. Residue appeared scorched.
N-chlorosuccinimide	134	28.1	0	21.6	39	Solids dissolved in $CHCl_3$.

TABLE 6. REACTIVITY OF CANDIDATE DECON MATERIALS WITH GD [a]

Materials	Molecular Weight	5-Min Exposure Unreacted GD, [b,c] micrograms	60-Min Exposure Unreacted GD [b,c] micrograms	Remarks
Control (GD only)	159	912	-	
Sodium dichloroisocyanurate dihydrate	256	0	581	
Potassium dichloroisocyanurate	236	816	640	
Sodium dichloroisocyanurate	220	950	514	
1,3-Dibromo-5,5,-dimethyl hydantoin	286	945	511	Very slight yellow color formed when agent added
1,3-Dichloro-5,5-dimethyl hydantoin	197	855	-	
Bromochloro-5,5,-dimethyl hydantoin	241	913	-	No color observed when agent added
STB (Super Tropical Bleach)	256	325	-	
Chlorinated Trisodium Phosphate	882	948	-	
Calcium hypochlorite	215	256	324	
Lithium hypochlorite	58	666	-	
N-chlorosuccinimide	134	905	-	

[a] Preliminary screening test results (see discussion in body of report)

[b] About 1000 µm of agent used in each test

[c] Quantity of decon used was 20 times (mol weight basis) agent

reactants, especially with respect to the rapid development of the yellow-orange color with HD and the bromo-substituted hydantoins, and only a slight yellow color with the GD. The volatility of the G-agents is considerably greater than that of the HD, apparently resulting in the lower-than-expected and confusing values for the initial GD and GB tests using these test procedures.

For these reasons, a modified screening test was investigated for the GD and GB agents. In these tests the decon materials were exposed to chloroform solutions containing the agent. The solutions were sampled and analyzed for unreacted GB or GD after 5 min and after 60 min of exposure. These test procedures appeared to be less sensitive than the screening tests involving solid dry decon materials and neat agents. Therefore the procedure was again modified and the five decon materials which showed promise in the first preliminary screening tests were reevaluated but using larger amounts of reactants.

About 200-250 mg of solid decon was contacted with 5 µl of GD and GB. The procedure was the same as that described previously for HD except for quantities. The results of this screening are shown in Table 7. Again the amount of agent recovered in the control samples was less than expected (about 65% to 70% of applied agent). However, using the controls as a base for calculating decon effectiveness, calcium hypochlorite was the most efficient decon material for GD and GB. HTH was as effective as calcium hypochlorite with GB but not as effective with GD. In general, the decon materials appeared to be somewhat more effective against GB than GD. Only very slight yellow color was observed when the 1,3-dibromo-5,5-dimethyl hydantoin was contacted with GD or GB. The color did intensify on standing after dilution with chloroform.

Based on the screening tests carried out in this study, calcium hypochlorite was the material of choice with respect to decontaminating GD and GB, as well as HD. The sodium dichloroisocyanurate dihydrate (ACL56) was earlier shown to be effective as a decon for HD but shows only partial decon effectiveness for GB and GD. Consequently increased emphasis was placed on encapsulation of calcium hypochlorite, with more limited emphasis on the ACL56. Further work with HTH and STB was curtailed because these are non-homogeneous mixtures of different kinds of particulate materials, unlike calcium hypochlorite and ACL56.

Further Study of Decon-CWA Reactions--The screening tests, discussed above, were carried out as single experiments. To confirm the screening results and to gain some insight with regard to reproducibility of these tests in light of the small quantities and restricted handling techniques, selected evaluations were run in triplicate. These evaluations included calcium hypochlorite with GD, GB, and HD; ACL56 with GD, GB, and HD; and

TABLE 7. REACTIVITY OF CANDIDATE DECON MATERIALS WITH GD AND GB[a]

Materials	Molecular Weight	Unreacted GD[b]				Unreacted GB[b]			
		5-Min Exposure		60-Min Exposure		5-Min Exposure		60-Min Exposure	
		micrograms	%[c]	micrograms	%[c]	micrograms	%[c]	micrograms	%[c]
Control (Agent Only)[d]	159	3280	100	3690	100	3340	100	3640	100
Calcium hypochlorite	215	1280	39	870	24	610	18	310	8.5
Sodium dichloroisocyanurate dihydrate	256	3700	100	3160	86	2670	83	2970	82
1,3-dibromo-5,5-dimethyl hydantoin	286	3110	95	3620	98	3410	100	2690	74
STB (Super Tropical Bleach)	256	2880	88	2920	79	2250	67	1800	49
HTH (High Test Hypochlorate)	215	2580	79	1600	43	510	15	300	8.2

a Screening test results (see discussion in body of report)

b About 5000 µg of agent used in each test. Quantity of decon used (mol. weight basis) was 20 times agent

c Based on control (agent only)

d Even though only 6.5% to 74% of CWA controls were recovered as determined by analysis, the control determinations were set at 100% for purposes of calculation and comparison of decon testing. See body of report for further details.

TABLE 8. REACTIVITY OF CANDIDATE DECON MATERIALS WITH CWA

Material	Unreacted GD [a]		Unreacted GB [a]		Unreacted HD [a]	
	Micrograms	Percent [b]	Micrograms	Percent [b]	Micrograms	Percent [b]
Control Agent Only	5370	100	3700	73	4180	74
	4760	95	3120	61	4740	84
	4290	86	3410	67	4660	83
average	4810	94	3410	67	4530	80
standard deviation	440	--	240	--	250	--
Calcium Hypochlorite	950	20	320	9.4	-0- [c]	-0-
	710	15	380	11.1	-0-	-0-
	1450	30	560	16.4	-0-	-0-
average	1040	22	420	12.3		
standard deviation	310	--	102	--		
Sodium Dichloroisocyanurate Dihydrate	4640	96	2480	73	-0-	-0-
	2890	60	2590	76	-0-	-0-
	3420	71	3340	98	-0-	-0-
average	3650	76	2800	82		
standard deviation	730	--	380	--		
1,3-dibromo-5,5-dimethyl hydantoin	--	--	--	--	-0- [d]	-0-
					-0-	-0-
					-0-	-0-

[a] About 5000 µm of agent used in each test. Quantity of decon used (mol. weight basis) was 20 times agent. Contact time was 5 minutes.

[b] Based on control (agent only).

[c] Vigorous reaction. See text for details.

[d] Formed an orange-red color.

1,3-dibromo-5,5-dimethyl hydantoin with HD. The results of these evaluations, using 5 μl of CWA and about 200 mg of decon materials, are shown in Table 3.

Against HD, all decons evaluated were completely effective. Of the three tests using calcium hypochlorite with HD, one resulted in no visible reaction, one resulted in spontaneous generation of a quantity of white smoke, and one resulted in a discernible flash of flame and audible snap. However, in each case, decon was complete. With DBDMH, an orange-red color was formed immediately on contact with HD.

With GD and GB, the calcium hypochlorite and ACL56 confirmed the results observed in the screening tests. The calcium hypochlorite was quite effective (78-88%) against both GD and GB. The ACL56 was only partially effective (18-24%) in deconning GB and GD.

It seems somewhat inconsistent that a material would decon ~80% of a CWA and not react with the remaining 20% when about 20-fold excess of decon is present. The same argument could be used for the 20% reaction level. Possibly the "geometry" of the experiment may be a limiting factor. Five microliters of liquid forms a very small drop and that is applied to relatively many small solid particles. The interfacial properties of two contacting materials may not be favorable to complete dispersion of the agent. Thus, a small quantity (say 20%) may not be contacted by decon. Where 20% of the CWA is deconned, reaction with the CWA may render the decon particles more sorptive of CWA and thus remove it for further contact with other decon particles.

Preliminary Indicator Materials Studies

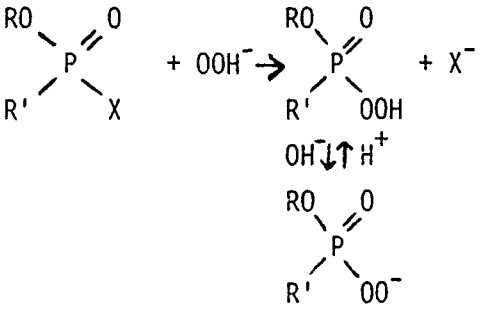
Although the major thrust of this project was the development of an effective encapsulated -OCl⁻ type decon, visual indication of the presence of agent is highly desirable in order to identify contaminated sites on the skin of personnel being treated. Consequently, some study of encapsulated indicator systems was included in the BCL efforts. The following paragraphs discuss several candidates and approaches for these indicator systems.

Indicator for HD Agent--The dibromo- and bromochloro-dimethyl hydantoins have been found to effectively decon HD (mustard) and to also provide intense color on contact with HD. This observation suggests that these materials may serve not only as a decon for HD, but also as indicators. To prevent contact with the skin of treated personnel, it will probably be desirable to retain, in the capsule, any free bromine or other reaction products formed in the color development. It is reasonable to consider that the coatings selected to encapsulate the decon will also serve to encapsulate the reaction products. Consequently, incorporation of dibromo- and/or bromochloro-dimethyl hydantoins in capsules was planned for Task 3 efforts.

Indicators for G Agents--The hydantoins also show slight coloration with GD, but the color is not as intense as desired for an effective indicator. Therefore, other indicator systems were considered and explored for the G agents.

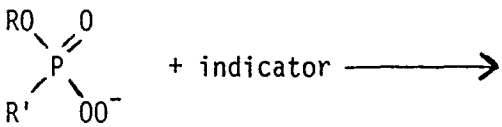
Both chemical and enzymatic methods have been used to detect the presence or absence of G-agents. However, the most highly developed techniques for the detection of G-agents are the chemical tests. Of these chemical tests described in the literature reviewed, four tests appeared to offer the best chance of developing an indicator system; i.e., the Schoenemann reaction, a chemiluminescent method, a fluorometric method, and a diisonitrosoacetone method.

The reaction, known as the Schoenemann reaction, is based upon the principle that perphosphonates oxidize amines (or other types of indicators) at much faster rates than do the peroxides alone. The formation of perphosphonic acid is considered to be the initial step (Step 1).



(Step 1)

The perphosphonate amine, which is in equilibrium with the perphosphonic acid in alkaline solution, oxidizes an indicator to give a colored, fluorescent, or chemiluminescent product (Step 2), depending on the specific materials involved.



(Step 2)

The perhydroxyl ions that can be considered are sodium perborate or sodium pyrophosphate peroxide. The colorimetric indicators include o-tolidine, o-dianisidine, leucotriaryl-methane compounds, benzidine, and o-ethoxy-o-sulpho-p-amino diphenylamine (compound #34).

The chemiluminescent test is similar to the Schoenemann reaction and involves sodium perborate, as the oxidant, and 5-amino-2,3-dihydro 1,4-phthalazine-dione (luminol) as the indicator.

The fluorometric method, which is also similar to the Schoenemann reaction, is based upon the formation of a highly fluorescent solution of indoxyl by the oxidation of indole by perphosphonate.

In the diisonitrosoacetone method, the diisonitrosoacetone reacts rapidly with G-agents in a weakly alkaline solution to yield hydrocyanic acid and an unidentified, intensely colored magenta compound. The method can be made more sensitive by adding certain compounds, e.g., o-dianisidine, o-tolidine, p-aminodiphenylamine, and aminopyridine. Along these same lines, an agent indicator crayon was previously developed which contained diisonitrosoacetone, o-tolidine, urea, lithium stearate, lithium chloride, and calcium oxide.

In considering these reactions and tests, BCL staff believed that encapsulation technology may be of value in developing an acceptable indicator system. The plan for utilizing encapsulation technology in the development of an indicator system was as follows (shown schematically in Figure 4, using the Schoenemann reaction as an example).

(1) The amine would be encapsulated separately in prills, i.e., the amine would be dispersed in a polymer bead matrix.

(2) The prills obtained in (1) would be incorporated in a second capsule, i.e., the second capsule system would contain a suspension of the prills (containing the amine) dispersed in an alkaline perborate solution.

(3) Capsules produced in (2) would then be totally dehydrated to a dry powder.

Following application of the dried capsules to a contaminated surface (as a dry powder), a water mist would be sprayed onto the dehydrated capsules. The dried capsules would rehydrate and the G-agents, which are readily water soluble, would permeate the capsule wall and react with the alkaline perborate solution. The prills would begin releasing the amine component, thus completing the reaction. The final indicator capsule system would be based upon a colored by-product, as described above, a chemiluminescent capsule product, or a fluorescent capsule product.

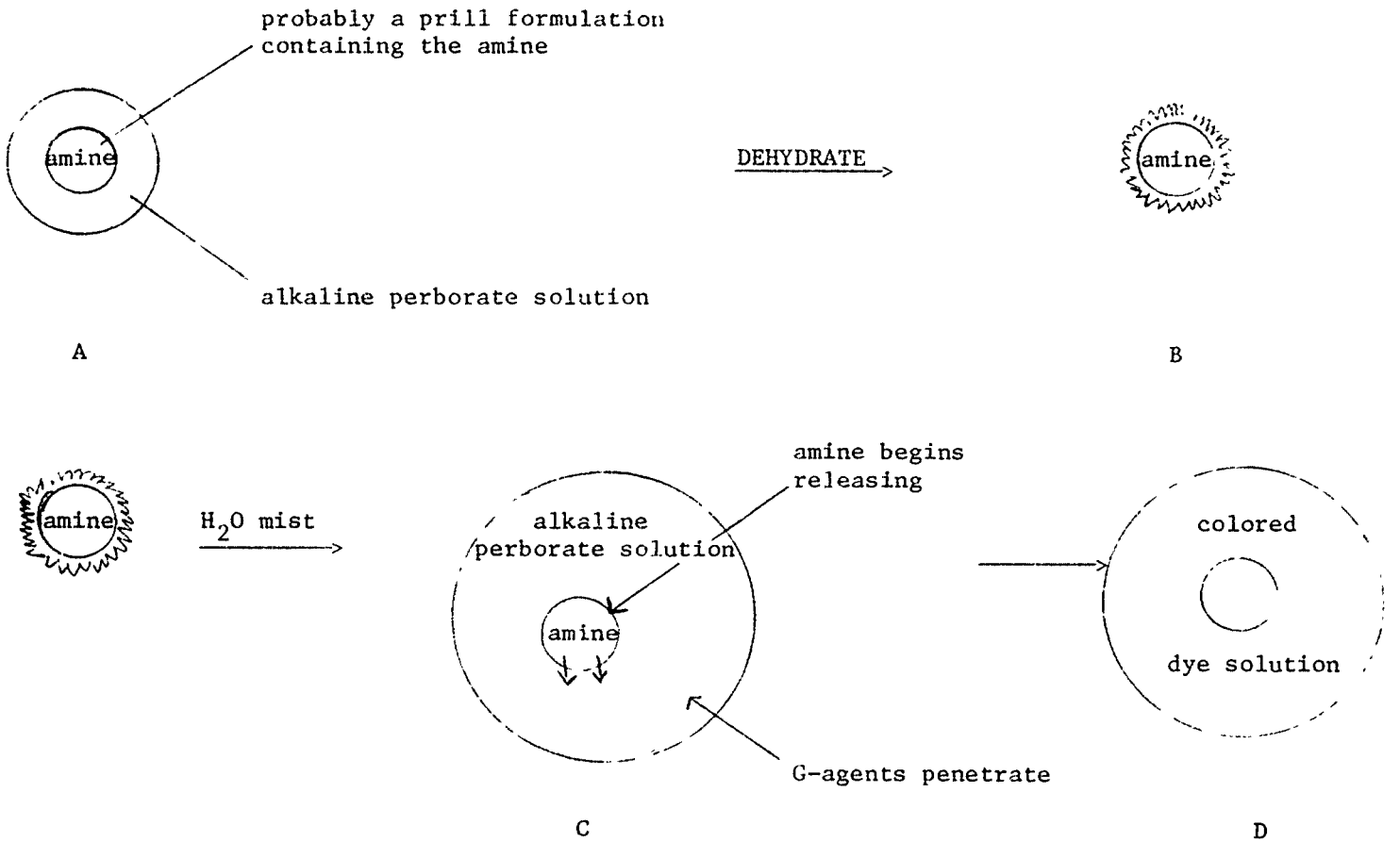


Figure 4. Schematic for development of an indicator capsule system.

Indicator capsules, as described, would need to be blended with separate decon capsules. The latter would contain one or more of the $-OCl^-$ materials. If both kinds of capsules are relatively small and are well mixed or blended, the mixture should provide both decon activity and visual indication of contaminated areas.

Selection of Materials for Encapsulation Studies

Three $-OCl^-$ materials were initially selected for the encapsulated decon studies: sodium dichloroisocyanurate dihydrate, calcium hypochlorite, and STB. These materials were selected because they showed the most effective decon actions with GD in preliminary screening tests, as previously discussed (see pages 32, 35), and because they are also effective with HD. In addition, they did not show excessive reactivity with solvents and solvent-polymer combinations. Efforts were also planned and applied for the encapsulation of (1) the dibromo- and/or bromochlorodimethyl hydantoin for use as an HD indicator, and (2) G agent indicators. Later in the program the encapsulation efforts with the Olin HTH were curtailed because it appeared that this material is composed of a mixture of several kinds of granules, rather than single granules containing the various chemical components including $Ca(OCl)$. A possible similar limitation (non-homogeneity) was foreseen for the currently commercial STB (super tropical bleach) as a candidate decon capsule core material.

The candidate capsule wall materials selected for encapsulation trials were (1) cellulose acetate butyrate, (2) chlorinated rubber (Parlon®), (3) polyvinylidine copolymer (Saran®), and (4) polyvinyl butyral (Butvar®). These resins were chosen because they appear to absorb both HD and G agents readily, and yet release it, as shown by paper spot test. This test, summarized in Table 1, indicated that films of these polymers either softened on contact with CWA or allowed the CWA to pass through and wet an underlying paper. These observations suggested that agents should be quickly absorbed by these polymers, yet readily diffused to the encapsulated $-OCl^-$ material for decon activity.

These polymer choices appear to be essentially confirmed by solubility parameter comparisons discussed previously. The results of the study of polymer film absorption of CWA vapor, which was completed late in the program, also confirm the choice of chlorinated rubber and cellulose acetate butyrate, but not of polyvinyl butyral or polyvinylidine chloride copolymer.

Task 3a. Encapsulation Studies

Most encapsulation trials were made employing either a phase separation process or a fluidized bed process, though additional brief studies were made using spray drying encapsulation for coating small $Ca(OCl)_2$ particles with chlorinated rubber.

Organic Phase Separation Encapsulation Studies--Organic phase separation works on the basis of solubility and the formation of a polymer-rich phase and a polymer-poor phase when a nonsolvent is slowly added to a polymer solution. Many polymers are not sharply precipitated from solution when selected nonsolvents are added. Across a limited range of nonsolvent-to-solvent ratios, a standing mixture will separate into two liquid fractions. One will have a higher proportion of solvent and polymer, but relatively little nonsolvent. The other will be higher in nonsolvent with some solvent and relatively little polymer.

Phase-separation microencapsulation systems have been applied to a variety of polymers to prepare capsule walls. These polymers include cellulose esters (e.g., cellulose acetate, ethyl cellulose, and cellulose acetate butyrate), polyvinyl butyral, Saran®, chlorinated rubber, and polylactide.

Capsule diameters may range from a few μm to greater than 1 mm. At BCL, wall-to-core ratios have varied from less than 1:30 to about 1:3. These variations in particle size and wall thickness permit wide ranges of release rates and/or core protection.

Usually the system is used with aqueous cores or solid particles, but it has been applied to oil-in-water type emulsions and to dispersions of solids in water. Agglomeration can be a problem with some materials, especially with very small capsules. Conversely, precipitation of extraneous polymer can sometimes occur. It is occasionally possible to prevent agglomeration by spray drying the capsular slurry at some selected stage after the capsule wall has formed.

The phase separation encapsulation runs all used cellulose acetate butyrate (Eastman CAB 381-20) as the capsule wall material. The first several runs used sodium dichloroisocyanurate dihydrate (Monsanto ACL56) as the core material. Other runs were made with HTH and with $Ca(OCl_2)$ as core materials. Bleach particles were dispersed (by stirring) in a polymer solution. The nonsolvent was added slowly from a buret, with continued stirring. As phase separation occurred, the polymer rich phase coated (encapsulated) the bleach particles. Tables 9, 10 and 11 show quantities of materials used in various runs. With addition of more non-solvent, the fluid encapsulant hardened into polymeric capsule walls.

The ACL56 material was sieved to provide various particle size fractions. The 300-595 μm fraction was used in these initial phase

separation runs. The CAB 381-20 was dissolved in various solvents including dichloromethane, chloroform, and ethyl acetate, alone, in mixtures, or combined with either hexane or toluene. A sample of the 300-595 μm ACL56 particles was dispersed in the polymer solution by stirring. Selected nonsolvents (hexane, cyclohexane, petroleum ether, toluene, mineral spirits, or selected mixtures of these) were then added to phase out the resin. The variables studied are discussed in this section, and all of these variables can influence the effectiveness of the encapsulation process.

Encapsulation studies were continued with additional decon materials, i.e., HTH (proprietary calcium hypochlorite, Olin Corp.) and a commercial reagent grade of calcium hypochlorite (J.T. Baker Co.). The ACL56 and HTH decon materials were initially sieved into various particle size fractions. However, only the 300-595 μm fraction was used in initial phase separation trials. With the calcium hypochlorite, several size fractions were encapsulated, i.e., 45-74 μm, 74-150 μm, and 150-300 μm.

The encapsulation studies performed with each of the decon materials are listed in Tables 9, 10, and 11. Table 9 lists the encapsulation studies performed with ACL56, while Tables 10 and 11 list the encapsulation studies conducted with the two calcium hypochlorite materials. It can be seen from these tables that a number of variables were examined in the encapsulation studies. These variables included (1) solvent type, (2) nonsolvent type, (3) ratios of solvent to nonsolvent, (4) polymer concentration in solution, (5) rate of nonsolvent addition, (6) particle size encapsulated, (7) stirrer speed, (8) core to wall ratio, and (9) effect of solvent/nonsolvent evaporation.

The use of cellulose acetate butyrate (CAB 381-20) as the wall material and the organic phase separation process as the encapsulation technique resulted in the successful encapsulation of all of these decon materials.

Fluidized Bed Encapsulation Studies--Fluidized bed microencapsulation is performed using fluidized bed process equipment, often called, simply, a fluidized bed (FB). A typical FB is a modified vertical column, usually circular or rectangular in cross section. Near the base is a plenum chamber where air or fluidizing gas is admitted. Above this is a distributor plate, which may be a section of screen, porous metal, or drilled plate. The distributor plate distributes the gas flow uniformly across the cross section of the column, and also prevents the bed material from falling into the plenum chamber. A fluidizing chamber is situated just above the distributor plate. This is the zone where solid particles are agitated and/or suspended in the moving gas stream. Above the fluidization chamber, the sides of the column taper outward, similar to an inverted, truncated cone or pyramid. The resulting, increasing cross section causes a decrease in velocity of fluidizing gas. With decreasing gas velocity, suspended particles fall back into the fluidizing chamber. Gas velocity (flow) is regulated to maintain a selected degree of particle agitation.

TABLE 9. ENCAPSULATION RUNS: ACL56

Run #	Polymer Code	Polymer, g	Core [a]	Solvents	Nonsolvents	Stirrer Setting	Results
1	CAB 381-20	5 0	20.0 g	375 ml Ethyl Acetate	a) 500 ml Toluene added to solvent b) 675 ml N-Hexane added over 19 min	2.0 (fast drive) triple blade	No walls observed Polymer precipitated as flakes, showing no affinity for particles.
2	CAB 381-20	5.0	20.0 g	375 ml Dichloro-methane	a) 75 ml N-Hexane added to solvent b) 450 ml N-Hexane added over 12.5 min.	2 0 (fast drive) triple blade	Some polymer coating particles; coating is not continuous and is very irregular. Most polymer present as flakes.
3	CAB 381-20	5.0	20.0 g	375 ml Dichloro-methane	a) 75 ml N-Hexane added to solvent b) 450 ml N-Hexane added over 60 min.	2.0 (fast drive) triple blade	Polymer present as gel-like masses on some of the particles.
4	CAB 381-20	5.0	20.0 g	375 ml Dichloro-methane	a) 75 ml N-Hexane added to solvent b) 450 ml N-Hexane added over 30 min.	1.5 (fast drive) triple blade	Continuous, smooth, regular walls observed on aqueous core droplets, lots of excess polymer, some capsules contain solid particles.
5	CAB 381-20	5.0	NOTE: This run was an attempt to enhance the polymer's affinity for the core particles by imbibing water on/in them. The details do not lend themselves to entrance in this table. The run was unsuccessful with the polymer precipitating as small granules. Details: Notebook #37984, page 10.			2.0 (fast drive) triple blade	
6	CAB 381-20	5.0	20.0 g	375 ml Dichloro-methane	a) 75 ml Cyclohexane added to solvent b) 450 ml Cyclohexane added over 12.5 min.	2.0 (fast drive) triple blade	Some polymer flakes adhering to particles, but no continuous wall.
7	CAB 381-20	1.25	5.0 g	94 ml Dichloro-methane	a) 19 ml N-Hexane added to solvent b) 825 ml N-Hexane added over 5.25 min.		Polymer precipitated as gel-like flakes with only small amount adhering to particles.
8	CAB 381-20	5.0	20.0 g	375 ml Chloro-form	a) 75 ml N-Hexane added to solvent b) 450 ml N-Hexane added over 12.5 min.	2.0 (fast drive) triple blade	Continuous wall observed on particles; very irregular, some agglomeration.
9	CAB 381-20	5.0	20.0 g	375 ml Chloro-form	a) 75 ml N-Hexane added to solvent b) 450 ml N-Hexane added over 58.5 min.	2.0 (fast drive) triple blade	Good conditions, regular walls observed, some chaff adhering to walls, slight agglomeration; N-Hexane appears the best non-solvent amoung those screened in quench vials; BEST RESULTS ACHIEVED SO FAR.

[a] All runs were made using a 300-595 μm sieve fraction of Monsanto ACL56 as the core material

TABLE 10. ENCAPSULATION RUNS OLIN HTH

Run #	Polymer Code	Polymer, g	Core [a]	Solvents	Nonsolvents	Stirrer Setting	Results
10	CAB 381-20	5 0	20 0 g	375 ml Chloroform	a) 75 ml N-Hexane added to solvent b) 450 ml N-Hexane added over 61 min.	2 0 (fast drive) triple blade	Continuous wall observed, irregular, very thin, agglomeration, lots of chaff
11	CAB 381-20	5 0	20 0 g	375 ml Chloroform	a) 75 ml Toluene added to solvent b) 450 ml N-Hexane added over 58 min	2 0 (fast drive) triple blade	Continuous wall observed, slightly irregular, very thin, agglomeration, lots of chaff, 1,1,1-Trichloroethane caused agglomeration in quench vials
12	CAB 381-20	5 0	20.0 g	75 ml Ethyl acetate, 375 ml Chloroform	a) 675 ml N-Hexane added over 91 min	2.0 (fast drive) triple blade	Continuous wall observed, regular, very thin, lots of chaff, wall "frizzy" with polymer strands adhering, agglomeration much reduced from runs 10, 11
13	CAB 381-20	5 0	20.0 g	25 ml Ethyl acetate, 375 ml Chloroform	a) 675 ml N-Hexane added over 22 min	2.0 (fast drive) triple blade	Thin, continuous coating observed chaff adhering, coating not "frizzy" as in run 12, serious agglomeration phase during run, greatly reduced at end
14	CAB 381-20	5 0	20 0 g	25 ml Ethyl acetate, 375 ml Chloroform	a) 675 ml N-Hexane added over 82 min	2 0 (fast drive) triple blade	Continuous, regular wall, some chaff adhering to particles, agglomeration midway through run, easing at end; lots of chaff in solution, amount of chaff adhering to particles lessened towards end of run
15	CAB 381-20	5 0	20 0 g	25 ml Ethyl acetate, 188 ml Chloroform, 187 ml Dichloromethane	a) 675 ml N-Hexane added over 87 min.	2 0 (fast drive) triple blade	Continuous, regular, smooth wall, little if any chaff adhering to particles, agglomeration much reduced BEST RUN SO FAR
16	CAB 381-20	5 0	20 0 g	25 ml Chloroform, 350 ml Dichloromethane	a) 450 ml N-Hexane added over 60 min	2.0 (fast drive) triple blade	No coating on particles observed throughout run, heavy polymer buildup on beaker
17	CAB 381-20	5 0	20 0 g	200 ml Chloroform, 200 ml Dichloromethane	a) 450 ml N-Hexane added over 57 min	2 0 (fast drive) triple blade	Continuous, uniform, smooth wall, some agglomeration during run, wall not as thick as run 15
18	CAB 381-20	5 0	20 0 g	75 ml Ethyl cetate, 150 ml Chloroform, 150 ml Dichloromethane	a) 675 ml N-Hexane added over 85 min	2 0 (fast drive) triple blade	Continuous, uniform, mostly smooth wall, slight chaff adhering to particles, no significant difference from run 15
19	CAB 381-20	3 75	15.0 g	19 ml Ethyl acetate; 141 ml Chloroform, 140 ml Dichloromethane	a) 507 ml N-Hexane added over 78 min	6 5 (slow drive) spiral-wound blade	NOTE 1000 ml Berzelius beaker used, covered during run, continuous walls, not completely uniform and smooth-some chaff adhering to particles, some agglomeration, thicker wall than run 15, distinct walls not observed till later in run
20	CAB 381-20	7 5	15 0 g	19 ml Ethyl acetate, 151 ml Chloroform, 140 ml Dichloromethane	a) 507 ml N-Hexane added over 74 min	6 5 (slow drive) spiral-wound blade	NOTE 1000 ml Berzelius beaker used, very thin continuous walls, not completely smooth-chaff adhering, wall very nonuniform in many cases, particles observed on which no wall could be observed, agglomeration

[a] In all runs the core material used was a 300-595 μm sieve fraction of Olin HTH

TABLE 11. ENCAPSULATION RUNS: CALCIUM HYPOCHLORITE (REAGENT)

Run # [a]	Core	Nonsolvent	Stirrer Setting	Results
21	15.0 g $Ca(OCl)_2$; 45-74 μm fraction	507 ml N-Hexane added over 73 min.	6.5 (slow drive) spiral wound blade	NOTE: 1000 ml Berzelius beaker used, covered; continuous walls, smooth, not completely uniform; mostly aggregates of 2-6 particles; slight chaff; only slight build-up on beaker.
22	15.0 g $Ca(OCl)_2$; 74-150 μm fraction	507 ml N-Hexane added over 70 min.	6.5 (slow drive) spiral wound blade	NOTE: 1000 ml Berzelius beaker used, covered; continuous walls, smooth, not completely uniform; mostly aggregates 2-6 particles; chaff present; agglomeration increased beyond 48 min.
23	15.0 g $Ca(OCl)_2$; 150-300 μm fraction	338 ml N-Hexane added over 49 min.	6.5 (slow drive) spiral wound blade	NOTE: 1000 ml Berzelius beaker used, covered, in general, results similar to runs 21 and 22; observed no significant difference in wall thickness/free polymer with varying core particle size between these three runs, i.e., 21-23.

a In each run the wall-forming polymer solution was composed of 3.75 g CAB 381-20 dissolved in a mixed solution composed of 79 ml ethyl acetate, 141 ml chloroform, and 140 ml dichloromethane.

Runs 21, 22 and 23 in this series are further identified as 37984-43, and -46 and -48 respectively.

There are several types of FB equipment. The one used for preparing microcapsules in this study is a modified Wurster column FB. The outer column of the fluidization chamber is circular in cross section. Centered in the fluidization chamber is a second cylindrical section which acts as a separator, creating inner and outer compartments. This separator is adjusted so that its base is located about 5/8 $\pm$ 3/8 inch above the distributor plate. A spray nozzle is mounted through the center of the distributor plate and protrudes up into the inner FB chamber. Gas flows are adjusted so the solid particles flow upward in the center section, where they are sprayed with coating solution. The wetted particles are propelled upward into the expanded, defluidizing zone and solvent evaporates. These lightly coated particles fall downward, in a fountain or umbrella-like pattern, into the outer (annular) fluidization chamber. This outer chamber has a lower gas velocity than the inner chamber so the next movement of particles is downward (though with agitation) in the outer chamber and upward in the inner chamber. Adjusting the height of the separator helps regulate the movement of particles from the outer chamber to the inner chamber. Repeated passes of particles through the coating zone results in gradual coating buildup and microencapsulation.

Fluidized bed encapsulation runs were made in the modified Wurster® fluidized bed (6 inch) using 900-1000 g batches of core particles. For all runs, the core particles were sieved, and the 300-595 μm fraction used. Most runs used the sodium dichloroisocyanurate dihydrate (Monsanto ACL56) as core particles, but the 38388-18-1, -2, and -3 trials used $Ca(OCl)_2$ particles. All runs were made at 1 to 16°C using predried air as the fluidizing gas. Solvent evaporation from the polymer solution sprayed onto the fluidized particles caused a bed temperature drop of several degrees centigrade below ambient (19°to 25°C). For all runs, fluidization was continued for about 10 min after completion of coating application to evaporate residual solvents. Microscopic examination of capsules thus prepared showed clearly defined walls, especially obvious with wall coating add-ons of 10% or more.

A total of 24 different capsule samples were prepared by this process (see Table 12). Runs 38388-5-2, -5-3, -18-2, -18-3, and -20-2 have DBDMH incorporated in the capsule walls. Figure 5 is a schematic of capsules from run 38388-5-3. The FB encapsulation series provides a basis for comparison of four different coatings on the ACL56 core particles: cellulose acetate butyrate (Eastman CAB381-20), chlorinated rubber (Hercules Parlon® S125), polyvinyl butyral (Monsanto Butvar® B73), and polyvinylidine copolymer (Dow Chemical Company, Saran® F310). It also provides capsule samples to compare core materials (38388-5-1) with ACL56 cores and 38388-18-1 with $Ca(OCl)_2$ cores with Parlon® walls), and capsule wall thickness (percent coating).

Runs 38388-20-1 and -20-2 were made to demonstrate that magnetite can be incorporated in capsule walls. As expected, this technique was successful in making the capsules sufficiently magnetic that they are

TABLE 12. FLUIDIZED BED ENCAPSULATION RUNS: CAPSULE COMPOSITION [a]

Run Number	Core Material [b] (%)	Polymer Coating [c] (Type)	(%)	Solvents Used (Type)	Coating Additive (Type)	(%)
37982-34-1	95	CAB 381-20	5	CH_2Cl_2	Red Dye	Trace
-2	90	"	10	"	"	"
-3	85	"	15	"	"	"
-4	80	"	20	"	"	"
-5	75	"	25	"	"	"
37982-37-1	95	Parlon® S125	5	CH_2Cl_2	Red Dye	Trace
-2	90	"	10	"	"	"
-3	85	"	15	"	"	"
38388-5-1	90	Parlon® S125	10	CH_2Cl_2	None	-
-2	87	"	11.5	"	DBDMH [c]	1.5
-3	82	"	16.5	"	"	1.5
38388-7-1	95	CAB 381-20	5	CH_2Cl_2	None	-
-2	90	"	10	"	"	-
-3	85	"	15	"	"	-
38388-8-1	95	Butvar® B73	5	d	None	-
-2	90	"	10	d	"	-
-3	84	"	16	d	"	-
38388-10-1	95	Saran® F310	5	e	None	-
-2	90	"	10	e	"	-
38388-18-1	90	Parlon® S125	10	CH_2Cl_2	None	-
-2	84	"	13	"	DBDMH [c]	3
-3	79	"	18	"	"	3
38388-20-1	85.4	Parlon® S125	4.8	CH_2Cl_2	Magnetite [c]	9.8
-2	78.6	"	8.6	"	Magnetite [c] + DBDMH [c]	8.0 + 4.7

[a] Encapsulation runs made in modified 6-inch Wurster type fluidized bed.
[b] Runs 38388-18-1, -2, -3 used $Ca(OCl)_2$. All other used ACL56. Core particles 300-595 μm.
[c] See text for description of materials.
[d] Mixture of CH_2Cl_2/EtOH/Toluene in 310/31/20 ratio.
[e] Mixture of CH_2Cl_2/MEK in 4/3 ratio.

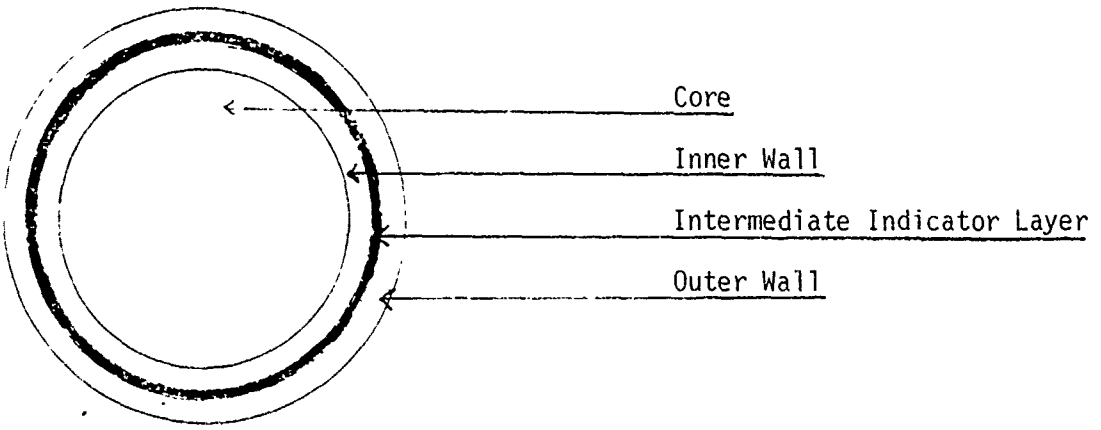


Figure 5. Schematic of 38388-5-3 multi-wall indicator-decon capsule*

Core --- sodium dichloroisocyanurate dihydrate (Monsanto ACL56) particle

Inner Wall --- chlorinated rubber (Parlon® S125) equal to approximately 10 % of core (by weight)

Intermediate Indicator Layer --- one-to-one ratio (by weight) of Parlon® S125 and DBDMH equal to approximately 3% of core (by weight)

Outer Wall --- Parlon® S125 equal to approximately 5% of core (by weight)

* Note: ACL56 particles are not actually spherical, but are irregular shapes. Circles are used here to more easily depict the basic concept.

attracted to a small magnet. Magnetic capsules may provide a means of recovering decon capsules from wounds.

Encapsulation by Spray Drying--Several trials were made in an effort to prepare microcapsules by spray drying using a CH_2Cl_2 solution of Parlon® S125 as the wall-forming phase for $Ca(OCl)_2$ particles ($\leq$ 74 μm) as the core material. Core to polymer ratios from 1:1 to 3:1 were attempted at various levels of dilution with solvent. All trials produced some threads, fibers, and irregular masses as well as some nicely coated particles and bits of superfluous polymer. None of the trials, however, produced a fully acceptable product although one system was selected for testing with agent.

Indicator Development and Encapsulation Studies

Several indicator systems have been studied as part of the encapsulation efforts. The DBDMH appears promising for use as an HD indicator as previously mentioned on page 39. Also, 2-napthol has been found to develop a visible color with the indole-perborate system. The details of these efforts are discussed next.

Indicator Materials Solubilities--Indicator capsule systems based upon either a chemiluminescent or fluorescent capsule product were selected for study. Luminol is the indicator associated with the chemiluminescent reaction and indole is associated with the fluorescent reaction. The perhydroxyl ions (providing proper alkalinity) are supplied by sodium perborate in both of these reactions. Thus, in preliminary studies, some basic solubility data was obtained for both luminol and indole. Table 13 lists the "gross" solubility data obtained.

Although 100 mg of luminol was only slightly soluble in a 1% sodium perborate solution, it became readily soluble when trisodium phosphate was added. However, when this test was performed only 50 mg of luminol was used in a 0.01% sodium perborate solution. Thus, although it appears the trisodium phosphate increased luminol solubility, additional studies should be performed since the luminol and sodium perborate concentrations were not equivalent in these tests.

Indole was also examined for its solubility in the following aqueous solutions:

(1) 1% sodium perborate/1% ethylene glycol[a]
(2) 1% sodium perborate/5% ethylene glycol[b]
(3) 1% sodium perborate/1% glycerol
(4) 1% sodium perborate/5% glycerol
(5) 1% sodium perborate/5% tetraethylene glycol

TABLE 13. SOLUBILITY OF LUMINOL AND INDOLE IN VARIOUS MEDIA AT ROOM TEMPERATURES

Media	Luminol	Indole
Distilled water	IS [a]	IS
Glycerol	IS	IS
Ethylene glycol	SlS [b]	RS [c]
1% Sodium perborate [d]	SS [e]	IS

[a] IS = insoluble
[b] SlS = slowly soluble
[c] RS = readily soluble
[d] 0.1 g of luminol or indole was added to 9.9 g of a 1% aqueous sodium perborate solution
[e] SS = slightly soluble

[a]9.8 g of a 1% sodium perborate solution
0.1 g of ethylene glycol
0.1 g of indole

[b]9.4 g of 1% sodium perborate solution
0.5 g of ethylene glycol
0.1 g of indole.

Indole was not soluble in any of the above solutions.

A follow-up study on indole solubility involved exposing 100 mg of indole to varying concentrations of ethylene glycol and glycerol. These results are presented in Table 14. The only method found for solubilizing indole at a relatively rapid rate in glycerol was to first solubilize the indole in acetone or 200 proof ethanol. Glycerol was then added to the acetone or ethanol solution with rapid mixing. The acetone or ethanol was then evaporated with continued stirring. Residual solvent was removed by placing the indole/glycerol solution in a vacuum oven for ~1 hour. A resultant clear solution of indole in glycerol was achieved, i.e., 10 mg indole/ml glycerol.

Preparation of Indicator Prills--Six batches of indicator-containing prills were prepared for later incorporation into indicator system microcapsules. Luminol and indole were selected as indicator materials. Disonitrosoacetone was also considered but later excluded because with GB and GD it produces hydocyanic acid as a reaction product, which is also very toxic and potentially lethal. Other indicator and color enhancing materials considered included o-dianisidine, o-tolidine, and amino-pyridine. These were excluded from further study and development because of their suspected carcinogenic potential.

Each of the six batches was composed of 1% (by weight) indicator and 99% matrix (carrier). The three different matrix materials used were (1) polycaprolactone polyol (Union Carbide's PCP0260), (2) polyethylene glycol (Union Carbide's Carbowax® 8000) and (3) Castorwax® (a castor oil derivative from Cas Chem, Inc.) These three waxy materials have considerably different degrees of water sensitivity. The Carbowax® is water soluble. The PCP0260 is water sensitive but not water soluble, and the Castorwax is a good water barrier material. Each matrix material was combined in hot melt with each indicator (luminol and indole) to provide six combinations. These hot melt systems were then prilled to produce spherical beads. Each batch of prills was sieved into four fractions: <150 µm, 150-300 µm, 300-600 µm, and >600 µm. These prills were used for later encapsulation studies.

Evaluation of Luminol Prills--One objective of these studies was to determine if the indicator was released from these prills. The leaching test for luminol indicator prills was performed by placing 1 g of the prills (containing 0.5% luminol) in 10 ml of the leaching solution. The

TABLE 14. INDOLE SOLUBILITY IN VARYING CONCENTRATION OF GLYCEROL AND ETHYLENE GLYCOL SOLUTIONS [a]

Concentration, Percent	Ethylene Glycol	Glycerol
5	Possibly partial solubility after 30 min	No solubility after 30 min
10	Possibly partial solubility after 30 min	No solubility after 30 min
20	Possibly partial solubility after 30 min	No solubility after 30 min
40	∿ 75% dissolved after 30 min	Partial solubility after 1.5 hr
60	Mostly dissolved after 5 min	∿50% dissolved after 1.5 hr
80	Dissolved in less than 3 min	Mostly dissolved after 1.5 hr

[a] 9 ml of the percent [b] glycerol or ethylene glycol solution
1 ml of a 1% sodium perborate solution (aqueous)
Add 100 mg of indole to the combined 10 ml solution.

[b] Percent = 5,10,20,40,60, or 80 with water.

size range of the prills tested was 150-425 μm diameter. The leaching solution contained 1 mg of sodium perborate and 10 mg of trisodium phosphate/10 ml of distilled water. Leaching tests were performed at 1, 2, 5, and 10 min of exposure.

One drop of a 1% cupric chloride/distilled water solution was added to the filtrate collected at the end of the leaching test. Cupric chloride gave a false positive test and the intensity of the chemiluminescent reaction was rated on a scale of 1 to 10, with 10 being very intense. The results of the leaching tests for prills containing luminol are presented in Table 15.

The results from Table 15 indicate that there is some luminol on, or close to, the outer surface of the prill. However, there is no doubt that luminol is being released from the prills, especially the PCP 0260 prills. The Carbowax 8000 prills released the luminol very rapidly, but they really had no integrity, i.e., they fell apart and dissolved.

Evaluation of Indole Prills--Based upon the indole solubility studies involving ethylene glycol and glycerol (discussed previously in this report), efforts to develop a fluorescent reaction were carried out. To observe the fluorescence, a small hand-held UV light (Mineral light, UVSL-25) was used. The "long wave" setting was used in these observations. To conduct these studies, 100 mg of indole was added to 10 ml solutions containing 9 ml of either a 5% or 80% ethylene glycol or glycerol solution and 1 ml of a 1% sodium perborate solution. Each total solution was agitated for 10 min. A series of four indole solutions was prepared by adding 100 mg indole and 1 ml of a 1% sodium perborate solution (aqueous) to 9 ml of each of the following: 5% ethylene glycol in water, 80% ethylene glycol in water, 5% glycerol in water, and 80% glycerol in water.

Following agitation, the solution was filtered and each filtrate was split into two vials. One drop of a 0.1% cupric chloride solution was added to one of the vials and the fluorescence observed. The results indicated that the blank vial (containing no cupric chloride) also produced fluorescence, i.e., the background fluorescence was considered too high to evaluate indole release from prills. Thus, based upon these observations, it was felt that another material, which would produce a false positive test, should be investigated.

TABLE 15. RESULTS OF LUMINOL PRILL LEACHING STUDIES

Prill Matrix	1 Min Preleach [a] /Leach	2 Min Preleach/Leach	5 Min Preleach/Leach	10 Min Preleach/Leach
Carbowax 8000	4/10 [b]	6/- [c]	-/-	-/-
PCP 0260	10/6	10/7	10/7	10/7
Castorwax	3/4	3/3	4/6	4/5

[a] Preleach - This is a 1-min filtrate which has been collected prior to the actual start of the leaching test, i.e., the prills were initially washed with a sodium perborate/trisodium phosphate/distilled water solution to remove any surface adsorbed luminol. The prills are then resuspended in fresh leaching solution for the actual defined time leach period.

[b] Intensity of chemiluminescence; a value of 10 being most intense.

[c] Prills fell apart; could not continue leach test.

In checking the literature[1] it was discovered that phthalic anhydride produces a reaction sensitivity similar to that of chemical warfare agents, i.e., it produces a (false) positive test in the fluorescent reaction. A similar test to that involving cupric chloride was conducted with phthalic anhydride. However, in these studies, a 0.1% phthalic anhydride-isopropanol solution was substituted for the 0.1% cupric chloride. The results of these studies indicated that the filtrate produced the desired fluorescence when 1 drop of 0.1% phthalic anhydride solution was added to one of two vials, one vial serving as a blank. The filtrate tested was obtained from the following reactants:

9 ml of a 5% glycerol-distilled water solution
1 ml of a 1% sodium perborate-distilled water solution
100 mg of indole

As a result, the prills (containing indole) were evaluated for their release of indole by placing 2.0 g of the prills (containing 0.5% indole by weight) in 10 ml of the test solution, i.e., 9 ml of a 5% glycerol-distilled water solution and 1 ml of a 1% sodium perborate-distilled water solution. If all of the indole was released from the 2 g of the prills, corresponding to 10 mg indole/10 ml of test solution, optimum development of the fluorescent reaction should occur. This concentration of indole was based upon literature sources[2] as providing optimum fluorescence. The results of these leach studies are presented in Table 16.

The results shown in Table 16 indicate that there is some indole on, or close to, the outer surface of the prill. However, there is essentially no indole being released from the prill as evidenced by no increase in the intensity of fluorescence with time.

The difference in release observed between luminol and indole prills may be related to the fact that when the prills were prepared, a

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1 "Development of A Multipurpose Kit. Search of Open Literature" Research Report 63-939-532-R1, May 31, 1963, F. P. Byrne (ed.) K. W. Guardipee, O. H. Kriege, R. J. McKeever and R. J. Nadilin, Contract No. DA18-108-AMC-115A.

2 "Detection and Estimation of Nerve Gases by Fluorescence Reaction", Bernard Gehauf and Jerome Goldenson, Analytical Chemistry, Vol. 29, No. 2.

TABLE 16. RESULTS OF INDOLE PRILL LEACHING STUDIES

Prill Matrix	1-min Preleach [a] /Leach	2-min Preleach/Leach	5-min Preleach/Leach	10-min Preleach/Leach
Carbowax 8000	10/- [b]	-/- [c]	-/- [c]	-/- [c]
PCP 0260	2/2	2/2	2/2	2/2
Castorwax	2/2	2/2	2/2	2/2

[a]Preleach - This is a 1-min filtrate which has been collected prior to the actual start of the leaching test; i.e, the prills were initially washed with a 5% glycerol - 1% sodium perborate distilled water solution to remove any surface adsorbed indole on the prills. The prills are then resuspended in fresh leaching solution for the actual defined time leach period.

[b]Intensity of fluorescence; a value of 10 being most intense.

[c]Prills fell apart; could not continue leach test.

melt blend of indole and polymer was formed; i.e., the prills were formed at 65-93°C while indole melts at 52-54°C. In the case of luminol, it may not have solubilized at the temperatures used in the preparation of the prills, i.e., luminol melts at 320°C. Thus, the luminol would have been dispersed as a homogeneous suspension of discrete particles in the prills. As the luminol is dissolved from the matrix, channeling probably occurs and further luminol may be released. This is not the case where the polymer matrix may have more thoroughly blended with the indole, perhaps forming a true solution.

Further examination of the literature[3] has disclosed the possibility of developing an indicator system which can be detected by a visible color change. In order to investigate this possibility, work was performed on developing an indole/2-napthol indicator system.

This reference indicated that the following ratio of reactants might be feasible in developing a visible color change:

100 mg indole 200 mg 2-napthol 10 ml ethanol	reactants

To examine this possibility, the following test was devised. One ml of the above reactants was mixed with 2 ml of a 1% sodium perborate-distilled water solution further diluted with 6 ml of distilled water. This volume was then split into two equal fractions. To one of the vials was added 25 drops of 0.1% phthalic anhydride simulant. To the other vial, 2 drops of glycerol were added and the solution mixed. This was followed by the addition of 25 drops of 0.1% phthalic anhydride. The following final concentrations of indole, 2-napthol and sodium perborate were examined using the above procedure:

Sample	Indole (mg/ml)	2-Napthol (mg/ml)	Sodium perborate (mg/ml)
A	1.1	2.2	2.2
B	1.1	4.4	2.2
C	2.2	1.1	2.2
D	4.4	1.1	2.2

3 "Analysis of GA by the Metalloid-Halogen Reaction. Preliminary Report", Bernard Gehauf and George B. Wilson, Army Chemical Center, T. D. M. R. No. 1307, Project A 1.13, Control Number 5004-1307, Feb. 28, 1947.

The addition of 2 drops of glycerol was shown to enhance color development. In addition, maximum color development (dark green) was obtained when the ratio of reactants in sample C were used. Increasing the number of glycerol drops, i.e., 4 and 6 drops, did not increase the color intensity using the ratio of reactants in sample C. However, increasing the concentration of simulant, i.e., phthalic anhydride, from 0.1% to either 0.3 or 0.5% did increase color intensity with sample C reactants. Thus, it might be feasible to develop a capsule indicator system based upon color development alone. Obviously, the color indicator capsule product would be preferred if sufficient color develops for visual detection.

Indicator Encapsulation Study--A core solution of the following components was encapsulated by an organic phase separation process using cellulose acetate butyrate (CAB) as the wall material: 4.4 mg indole and 2.2 mg 2-napthol in 2 ml of ethanol, 4 ml of a 1% aqueous sodium perborate, 470 mg of glycerol, and 12 ml of distilled water. The microcapsules were humid-air-dried to remove residual solvent from the capsule wall. However, when a 0.5% phthalic anhydride-isopropanol solution was placed on a sample of the capsules, no color change was observed. Previously a dark green color developed with this agent simulant.

It appeared that the solution used to phase out the polymer had probably extracted one of the core components, e.g., 2-napthol. Consequently, the post-loading of microcapsules, which contained only a distilled-H_2O core was investigated (to avoid possible loss of indicators into the encapsulation processing fluids). This was accomplished by placing 1.5 of either humid air-dried or dehydrated capsules in 9 ml of the following solution for 2 hr:

1 ml	indole (299 mg) 2-napthol (100 mg) 200 proof ethanol (10 ml)
2 ml	1% sodium perborate
6 ml	distilled water
4 drops	glycerol
9 ml	approximate total

However, once again, when the 0.5% phthalic anhydride-isopropanol solution was placed on a sample of post treated, filtered capsules, no color change development occurred. Thus, one of the components may not be transferring across the CAB wall within the allotted time of the post-loading process, or the CAB wall was masking any color development.

It was later found that indole is much more soluble in the organic solvents (used in the phase separation process) than in water (used in capsule cores). Consequently most of the indole, initially in the aqueous core solution, was probably transferred to the organic fluids during the

encapsulation process. Therefore, it was decided that a post-loading technique would be used to imbibe indole into prepared microcapsules. CAB microcapsules were prepared using 1.1 g of polymer for wall formation and a core containing 9.0 g of a 5% glycerol/H_2O solution plus 1.0 g of 1% sodium perborate/H_2O solution. After the capsules were prepared and filtered, they were humid-air-dried for several hours to remove residual solvents. In this process, residual solvent is removed without altering the core contents; i.e., the capsules retain their original diameter as achieved during their preparation. These capsules were then dispersed in a saturated aqueous indole solution (containing 1% sodium perborate) in order to post-load the capsule core by an equilibration (diffusion) process. Triton® X-100 was used to disperse the capsules in the aqueous solution. The capsules were rinsed with distilled water to remove any surface indole using a filtering and suction apparatus. The capsules were then removed from the filter paper and humid-air-dried for 1 hr.

A sample of these capsules was spread as a thin layer on a glass plate. Three single drops of saturated phthalic anhydride (aqueous) were placed at three different points among the spread capsule sample. The sample was then observed under UV light. After about 10 min, a definite fluorescence developed at the points where the phthalic anhydride solution had been added.

The results of this study are not definitive, but the concept does appear promising.

Task 3b. Capsule Evaluations

Indicator and decon capsules were evaluated with neat CWA. In addition, selected decon capsules were evaluated in leaching tests and in skin tests. The following sections describe these efforts.

Evaluation of Indicator Systems with Neat Agent--The purpose of this part of the effort was to evaluate the more promising indicator reactions using neat agent (GB and GD). Prior studies had shown that simulants provided the desired reactions with the fluorescent, color-change and chemiluminescent systems. The results of these studies, conducted at Battelle's Hazardous Materials Laboratory, are presented in Table 17. Of the indicator systems, the fluorescent system showed the most promise and appears especially promising with respect to a possible microcapsule system since a very small droplet in a glass capillary tube was easily detected.

Three different samples of Parlon® S125 chlorinated rubber encapsulated ACL56 were prepared by fluidized bed (FB) encapsulation: (1) ACL56 particles coated with 10% Parlon® S125, (2) ACL56 particles coated with

TABLE 17. INDICATOR REACTIONS: NEAT CWA'S[a] VS SIMULANTS

Indicator System	Simulant Concentration (μg/ml)[b]	Development Time[c]	Intensity[c]	Persistence[c]	Color Shade[c]	Capillary Visibility[d]
Indole Fluorescence	Phthalic Anhydride in Isopropanol (14)	Equal	Agent much more intense, GB more intense than GD[e]	Agent much longer, still intense, after 45 min	Equal	Very good (Both GB and GD)
Indole/2-Napthol Color Change	Phthalic Anhydride in Isopropanol (389)	Agent faster, GB faster than GD	Agent more intense initially equal after 5 min	Equal	Equal	Minimal (Both GB and GD)
Luminol Chemiluminescence	Aqueous Cupric Chloride (21)	---------- Simulant Gave Chemiluminescence, But Agents Did Not ----------				

[a]Both GB and GD tested. Results similar except as noted.

[b]Concentration in reactant solution.

[c]Relative: agent vs simulant.

[d]Indicating solution drawn into glass capillary tube, 1 mm I.D. rough simulation of small quantity in microcapsules.

[e]Difference in intensity, probably due to greater agent concentration in reactant solution.

Parlon® plus a second layer (3%) of a 1:1 ratio of Parlon® and DBDMH, and (3) ACL56 particles similar to (2) but with an added third layer (5%) composed of Parlon®. About 0.2 g of each material was treated with 5 μl of HD. There was no visible color development with the particles coated only with Parlon®. However, in both systems where DBDMH was present, an immediate yellow color was observed. This color appeared to deepen for about 5 sec and then remained constant. There was no qualitative difference in color development between the systems (2) and (3) described above. Thus, as anticipated from prior studies on this project the incorporation of DBDMH in the capsule wall appears to show considerable promise as an indicating decon for HD.

Evaluation of Encapsulated Decons--Twelve capsule samples were selected for testing with agent and are described in Table 18. Capsule samples 38388-5-1, -7-2, -8-2, and -10-2 were selected to compare the effects of four different coating materials. Other samples were selected to compare the effects of capsule size or encapsulation processes on the performance of the capsules when exposed to agent.

Test Procedure. To compare the effectiveness of -OCl- capsules in absorbing and decontaminating CW agents, the following test procedure was followed.

(1) Solid capsule samples were weighed into conical-bottom centrifuge tubes (quantity of -OCl⁻ material equal to about 20 moles per mole of agent).

(2) Five microliters of agent were added and the tubes capped.

(3) After 5 min 10 ml of hexane was added, mixed thoroughly, and allowed to remain in contact with the capsules for 1 min.

(4) 1.0 ml of the hexane solution was sampled and diluted with 2.0 ml of hexane for analysis by gas chromatography.

(5) The remaining hexane solution was decanted from the capsules and 10 ml of chloroform was added to the capsules in the tube, mixed thoroughly and allowed to remain in contact with the capsules for 5 min.

(6) The chloroform solution was centrifuged, if required, and 1.0 ml of the solution was sampled and diluted with 2.0 ml of chloroform for analysis.

(7) Steps (1) through (6) were repeated for fresh samples, but 60 min was allowed between addition of the agent and the hexane wash.

TABLE 18. DESCRIPTION OF CAPSULES SELECTED FOR CWA TESTING

Sample Number	Core Material		Coating/Wall Material		Encapsulation Process Used
	Type	Size (μm)	Type	Weight %	
38388-5-1	ACL56	300-595	Parlon®S125	10	Fluidized Bed
38388-5-2	ACL56	300-595	Parlon®S125	11.5	Fluidized Bed
			DBDMH[a]	1.5	
38388-7-2	ACL56	300-595	CAB381-20	10	Fluidized Bed
38388-8-2	ACL56	300-595	Butvar®B73	10	Fluidized Bed
38388-10-2	ACL56	300-595	Saran®	10	Fluidized Bed
38388-18-1	$Ca(OCl)_2$	300-595	Parlon®S125	10	Fluidized Bed
38388-18-2	$Ca(OCl)_2$	300-595	Parlon®S125	13	Fluidized Bed
			DBDMH[a]	3	
38388-14-1	$Ca(OCl)_2$	≤ 74	Parlon®S125	25	Spray Drying
37984-43	$Ca(OCl)_2$	45-74	CAB381-20	25	Phase Separation
37984-46	$Ca(OCl)_2$	74-150	CAB381-20	25	Phase Separation
37984-48	$Ca(OCl)_2$	150-300	CAB381-20	25	Phase Separation
37984-19	ACL56	300-595	CAB381-20	25	Phase Separation

[a]Dibromo-dimethyl-hydantoin.

The hexane extraction provides a measure of absorption efficiency of the capsule coating (a smaller amount of agent in the hexane extract indicates higher absorption of agent by the coating). The chloroform extract measures the permeation efficiency of the coating and decon effectiveness of the $-OCl^-$ material; i.e., a low agent content in the chloroform wash indicates good permeation and decon action. A higher content of agent, however, probably is indicative of high absorption of agent by the coating but low permeation.

HD-Microcapsule Test Results. Tables 19 through 23 detail the evaluation results obtained with the selected microcapsule systems with HD. Several capsule systems showed > 90% of HD deconned at 60 min and two showed > 85% of HD deconned at 5 min. The percent of HD from the hexane wash, plus the percent of HD from $CHCl_3$ wash, plus the "deconned" percent of HD equals 100% based on 5000 μg HD in each test. (A series of four controls showed 5003 ± 113 μg HD.) The hexane wash results include any HD that may have been on test tube surfaces as well as surface wash of the capsules. As noted previously the $CHCl_3$ wash percent HD is believed to represent HD absorbed in the capsule wall but not yet reacted. The "deconned percent of HD" is calculated by subtracting the total of the two solvent wash values from 100%.

Table 19 shows a comparison of effectiveness of the four selected wall materials used to coat (10% level) ACL56 particles (300-595 μm) in a fluidized bed. In this series, the Parlon® S125 (chlorinated rubber) coated capsules show the best overall performance, i.e., the lowest hexane percent of HD at both 5 and 60 min as well as the highest percent of HD deconned at both time periods (77.3% at 5 min and 96.9% at 60 min). However, the CAB 381-20 (cellulose acetate butyrate) capsules show results nearly as favorable as the Parlon® capsules. The Saran® coating was significantly less effective and the Butvar® B73 capsules showed poor absorbency and little deconning, especially at 5 min.

The test results shown in Table 20 provide a comparison of Parlon® coated ACL56 and $Ca(OCl)_2$ particles with Parlon®-DBDMH coatings as a second layer indicator. As expected, the capsules containing DBDMH showed a bright yellow color shortly after being contacted with HD (~15 sec). The color appeared to be the more intense with the $Ca(OCl)_2$ capsules coated with Parlon® and 3% of dibromo compound than with the ACL56 particles coated with Parlon® and 1.5% DBDMH. A white cloudy or smoky halo appeared above the $Ca(OCl)_2$ capsules on the sides of the tubes, especially with the 1-hr samples.

It appears that the incorporation of DBDMH in the surface layer of the coating (these two capsule samples have double walls) increased the absorption rate of HD and the rate of the decon activity. The data also suggest that increasing the thickness of the Parlon®-DBDMH layer increases the effectiveness. As noted, the DBDMH also serves as a visible indicator of HD because of its color change to a bright yellow when used in the

TABLE 19. HD-MICROCAPSULE EVALUATIONS, COMPARISON OF WALL MATERIALS: FLUIDIZED BED COATED ALC56 PARTICLES (300-595 μm) WITH 10% WALL MATERIAL

Type Wall Material	5-Min Test Results[a]			60-Min Test Results[a]		
	Hexane Wash % of HD	$CHCl_3$ Wash % of HD	Deconned % of HD	Hexane Wash % of HD	$CHCl_3$ Wash % of HD	Deconned % of HD
Parlon®S125	19.6	3.1	77.3	3.1	0	96.9
CAB381-20	21.1	8.1	70.8	4.1	0	95.9
Saran®	34.4	18.5	52.9	11.3	6.7	81.9
Butvar®B73	91.8	3.6	4.6	28.1	11.2	60.6

[a]Hexane wash plus $CHCl_3$ wash plus deconned equals 100%.

TABLE 20. HD-MICROCAPSULE EVALUATIONS: COMPARISON OF FLUIDIZED BED COATED ACL56 AND $Ca(OCl)_2$ PARTICLES (300-595 μm) WITH PARLON® AND PARLON® DBDMH WALL MATERIALS

Type Wall Material	Type Core Material	5-Min Test Results[a] Hexane Wash %	5-Min Test Results[a] $CHCl_3$ Wash %	5-Min Test Results[a] Deconned %	60-Min Test Results[a] Hexane Wash %	60-Min Test Results[a] $CHCl_3$ Wash %	60-Min Test Results[a] Deconned %
10% Parlon® S125	ACL56	19.6	3.1	77.3	3.1	0	96.9
10% Parlon® S125	$Ca(OCl)_2$	31.1	12.2	56.7	17.5	9.1	73.4
11-1/2% Parlon® S125 1-1/2% DBDMH[b]	ACL56	14.6	0	85.4	3.7	0	96.3
13% Parlon® S125 3% DBDMH[b]	$Ca(OCl)_2$	9.1	0	90.9	3.5	3.0	93.5

[a]Hexane wash plus $CHCl_3$ wash plus deconned equals 100%.

[b]Dibromo-dimethyl-hydantoin.

Parlon® capsule walls. Reasons for the specific differences in performance between the Parlon® coated ACL56 and Parlon® coated $Ca(OCl)_2$ particles are not presently known.

Table 21 shows comparative data for three sizes of $Ca(OCl)_2$ core particles coated with CAB 381-20 using phase separation encapsulation. There appears to be a clear trend towards more and faster absorption of HD with decreasing capsule size especially in the 5-min test. This same trend is also seen at 60 min for the three $Ca(OCl)_2$ capsules. All three samples of smaller size capsules show generally better deconning at 5 min and less decon effectiveness at 60 min than the larger ACL56 capsules. This latter observation may indicate that the quantity of $Ca(OCl)_2$ in the capsule core of the smaller capsules is insufficient to provide complete deconning of HD.

Table 22 compares two capsule systems with ACL56 cores and CAB 381-20 capsule walls. One capsule system has a 25% CAB capsule wall and was encapsulated by the phase separation process. The second system has a 10% CAB capsule wall and was encapsulated by a fluidized bed process. The performance/effectiveness at 60 min is similar for both samples. However, the 5-min samples show considerable differences, especially in the hexane wash (nonabsorbed HD) and the percent HD deconned. The complete reasons for these differences have not been established although the amount of wall present is obvious. It is suspected that the coating configuration is different for the two processes and that these differences may be more significant than those related to percent coating (coating thickness).

Table 23 compares spray dried capsules with capsules formed by phase separation. As described earlier in this report, even the best spray dried capsule samples contained fibers and irregular bits of polymer as well as "good" capsules. The spray dried capsules show rapid absorption of HD, similar to the smallest capsules from the phase separation series and similar totals for total deconning at 5 and 60 min.

Overall, the most effective deconning of HD is shown by capsules from runs 38388-5-1, -5-2, -7-2, and -18-2 (see Tables 18, 19, and 20). It appears that Parlon® is the best of the wall materials evaluated for both rate of absorbency at 5 min and more complete deconning at 60 min, although CAB also looks almost as promising when coated on ACL56 particles by fluidized bed (38388-7-2). Incorporation of DBDMH with Parlon® in the surface layer of the capsule wall further increases the absorption rate of HD, as well as providing visual color indication of the presence of HD. Thus, 38388-5-2 and -18-2 are presently considered to be the most promising capsules tested for HD deconning.

Test Results of Microcapsules with Neat GB and GD. Table 24 shows test results obtained with a series of capsules, with ACL56 cores and various polymer walls, treated with these agents. As expected from tests with non-encapsulated ACL56 and neat GB and GD, there was very little

TABLE 21. HD-MICROCAPSULE EVALUATIONS: $Ca(OCl)_2$ PARTICLES COATED WITH CAB 381-20 (25%) BY PHASE SEPARATION. COMPARISON OF CAPSULE SIZES

$Ca(OCl)_2$ Particle Size µm	5-Min Test Results[a]			60-Min Test Results[a]		
	Hexane Wash %	$CHCl_3$ Wash %	Deconned %	Hexane Wash %	$CHCl_3$ Wash %	Deconned %
45-74	13.1	23.6	63.2	11.5	16.6	71.9
74-150	20.8	22.1	57.0	12.5	7.3	80.3
150-300	40.8	13.1	46.1	30.1	8.0	62.0
300-595[b]	48.7	3.6	47.7	3.2	3.9	92.9

[a]Hexane wash plus $CHCL_3$ wash plus deconned equals 100%.

[b]ACL56 material rather than $Ca(OCl)_2$.

TABLE 22. HD-MICROCAPSULE EVALUATIONS: COMPARISON OF 10% AND 25% CAB381-20 WALLS ON ACL56 PARTICLES (300-595 μm)

% Wall	Encapsulation Process	5-Min Test Results[a]			60-Min Test Results[a]		
		Hexane Wash %	$CHCl_3$ Wash %	Deconned %	Hexane Wash %	$CHCl_3$ Wash %	Deconned %
25	Phase Separation	48.7	3.6	47.7	3.2	3.9	92.9
10	Fluidized Bed	21.1	8.1	70.8	4.1	0	95.9

[a]Hexane wash plus $CHCl_3$ wash plus deconned equals 100%.

TABLE 23. HD-MICROCAPSULE EVALUATIONS: $Ca(OCl)_2$ PARTICLES ENCAPSULATED IN PARLON® S125 BY SPRAY DRYING COMPARED WITH OTHER SELECTED MICROCAPSULES

$Ca(OCl)_2$ Particle Size µm	Encapsulation Process	Wall Material %	Wall Material Type	5-Min Test Results[a] Hexane Wash %	5-Min Test Results[a] $CHCl_3$ Wash %	5-Min Test Results[a] Deconned %	60-Min Test Results[a] Hexane Wash %	60-Min Test Results[a] $CHCl_3$ Wash %	60-Min Test Results[a] Deconned %
< 74	Spray Drying	25	Parlon®	8.5	31.1	60.4	6.7	20.2	73.2
45 -74	Phase Separation	25	CAB	13.1	23.6	63.2	11.5	16.6	71.9

[a]Hexane wash plus $CHCl_3$ wash plus deconned equals 100%.

TABLE 24. CWA-MICROCAPSULE EVALUATIONS, COMPARISON OF WALL MATERIALS: FLUIDIZED BED COATED ACL56 PARTICLES (300-595 μm) WITH 10% WALL MATERIAL

Type Wall Material	5-Min Test Results[a] Hexane Wash %	5-Min Test Results[a] $CHCl_3$ Wash %	5-Min Test Results[a] Deconned %	60-Min Test Results[a] Hexane Wash %	60-Min Test Results[a] $CHCl_3$ Wash %	60-Min Test Results[a] Deconned %
With GD						
Parlon®S125	90	15	a	77	27	a
CAB381-20	124	13	a	28	73	a
Saran®F310	66	42	a	22	67	11
Bu+	100	17	a	66	37	a
With GB						
Parlon®S125	58	33	9	46	48	6
CAB381-20	35	45	20	28	76	a
Saran®F310	15	71	14	14	101	a
Butvar®B73	77	37	a	57	57	a

[a]The % deconned is calculated by subtracting the sum of hexane wash % and $CHCl_3$ wash % from 100%. For these samples the sum of the wash % exceeded 100.

effective decon activity observed. The results shown in the hexane and $CHCl_3$ wash columns suggest that Saran® F310 and CAB 381-20 (cellulose acetate butyrate) are more absorbent to GB and GD than are Parlon® S125 and Butvar® B73. All four of the polymers show higher absorbence for GB than GD. It is not known why some tests showed greater than 100% recovery of agent in the hexane and $CHCl_3$ washes.

The data presented in Table 25 provides a comparison of fluidized bed Parlon®-coated capsules with those coated with Parlon®-DBDMH. The capsule cores are either ACL56 or $Ca(OCl)_2$ as indicated. While the presence of DBDMH in most of the capsule walls does not appear to significantly affect the total decon activity of the capsule, some of the hexane wash results do show definite decreases. Furthermore, the differences are greater with the $Ca(OCl)_2$ core capsules than with capsule cores containing ACL56 (Runs 38388-18-1 and -18-2 compared to runs 38388-5-1 and -5-2 described in Table 18). It has not been clearly established at this time whether these differences are due to the core material or to the thicker (6% vs. 3%) wall of 1:1 DBDMH/Parlon®. However, it appears likely that with GB and GD, the action of the DBDMH is primarily to increase the rate of agent absorption (i.e., less agent is "recovered" in the hexane wash especially at 5 min). These observations contrast with the observed effects with HD which showed an increase in decon effectiveness when DBDMH was included. These results, however, are consistent with results of tests with DBDMH and neat agents (HD, GB, and GD) as reported earlier, i.e., the DBDMH is an effective decon for HD but not for GB or GD. The increase in absorption rate suggests that incorporation of other selected materials in the capsule walls may further improve the absorption rates.

The data in Table 26 compares the decon activity of various $Ca(OCl)_2$ core sizes, coated with CAB 381-20 by the phase separation process. There is no clear trend of absorption rate (low hexane percent is interpreted as rapid agent absorption) or decon effectiveness as a function of capsule size with either GB or GD. The decon effectiveness at 60 min compares favorably with non-encapsulated $Ca(OCl)_2$, presented in Table 8, which shows 70% to 85% deconned for GD and 83% to 91% deconned for GB.

Table 27 compares ACL56-core particles coated with cellulose acetate butyrate polymer (CAB 381-20) prepared by two different encapsulation processes, i.e., phase separation and fluidized bed. In the GD 5-min test results, the hexane wash percent for the fluidized bed capsules is much higher than for the phase separation capsules, but the reverse is true with GB. The percent deconned is low probably from the low decon activity of the ACL56 cores with both GB and GD. In the 60-min test, the hexane wash percent figures are more uniform between agents and between capsule samples.

TABLE 25. CWA-MICROCAPSULE EVALUATIONS: COMPARISON OF FLUIDIZED BED COATED ACL56 AND $Ca(OCl)_2$ PARTICLES (300-595 μm) WITH PARLON® AND PARLON® UBDMH WALL MATERIALS

Type Wall Material	Type Core Material	5-Min Test Results[b] Hexane Wash %	5-Min Test Results[b] $CHCl_3$ Wash %	5-Min Test Results[b] Deconned %	60-Min Test Results[b] Hexane Wash %	60-Min Test Results[b] $CHCl_3$ Wash %	60-Min Test Results[b] Deconned %
With GD							
10% Parlon® S125	ACL56	90	15	b	77	27	b
10% Parlon® S125	$Ca(OCl)_2$	113	2	b	27	8	65
11-1/2% Parlon® S125 with 1-1/2% DBDMH[a]	ACL56	81	22	b	60	39	1
13% Parlon® S125 with 3% DBDMH[a]	$Ca(OCl)_2$	57	14	29	18	24	58
With GB							
10% Parlon® S125	ACL56	58	33	9	46	48	6
10% Parlon® S125	$Ca(OCl)_2$	86	16	b	14	10	76
11-1/2% Parlon® S125 with 1-1/2% DBDMH[a]	ACL56	56	47	b	46	50	4
13% Parlon® S125 with 3% DBDMH[a]	$Ca(OCl)_2$	18	17	65	5	15	80

[a] Dibromo-dimethyl-hydantoin.

[b] The % deconned is calculated by subtracting the sum of hexane wash % and $CHCl_3$ wash from 100%. For these samples the sum of wash % exceeded 100.

TABLE 26. CWA-MICROCAPSULE EVALUATIONS: $Ca(OCl)_2$ PARTICLES COATED WITH CAB381-20 (25%) BY PHASE SEPARATION. COMPARISON OF CAPSULE SIZES

$Ca(OCl)_2$ Particle Size μm	5-Min Test Results[a]			60-Min Test Results[a]		
	Hexane Wash %	$CHCl_3$ Wash %	Deconned %	Hexane Wash %	$CHCl_3$ Wash %	Deconned %
With GD						
45-74	41	13	46	23	16	61
74-150	31	13	56	15	10	75
150-300	66	15	19	26	8	66
With GB						
45-74	11	27	62	5	16	79
74-150	58	25	17	14	17	69
150-300	16	12	72	16	16	68

[a]Hexane wash plus $CHCl_3$ wash plus deconned equals 100%.

TABLE 27. CWA-MICROCAPSULE EVALUATIONS: COMPARISON OF 10% AND 25% CAB381-20 WALLS ON ACL56 PARTICLES (300-595 μm)

% Wall	Encapsulation Process	5-Min Test Results[a]			60-Min Test Results[a]		
		Hexane Wash %	$CHCl_3$ Wash %	Deconned %	Hexane Wash %	$CHCl_3$ Wash %	Deconned %
With GD							
25	Phase Separation	41	30	29	34	63	3
10	Fluidized Bed	124	3	a	28	73	a
With GB							
25	Phase Separation	58	20	22	40	19	41
10	Fluidized Bed	35	45	20	28	76	a

[a]The % deconned is calculated by subtracting the sum of hexane wash % and $CHCl_3$ wash % from 100%. For these samples the sum of wash % exceeded 100.

In Table 28, $Ca(OCl)_2$ particles encapsulated with Parlon® by spray drying are compared to $Ca(OCl)_2$ particles encapsulated with CAB 381-20 by phase separation. The 5-min hexane wash figures for Parlon® are similar to those in Table 24, but the 60-min test results for Parlon® in Table 28 were much lower. This may be due to the smaller particle size of the spray dried capsules vs. the fluidized bed capsules. As noted earlier in Table 24, the CAB wall material shows faster absorption for GB and GD than does Parlon®. In addition, the decon effectiveness at 5 min is much higher for the CAB capsules than the Parlon®, although the $CHCl_3$ wash figures are nearly equal, suggesting similar permeation rates.

As noted previously, the spray dried capsules include bits of fiber, filaments and "fuzz", as well as good capsules. Such polymer fragments (not containing any decon material) would probably provide minimal decon activity. Consequently, some portion of the agents would likely become trapped in such fragments, and this entrapment may account for the lower 60-min percent deconned data for the spray-dried Parlon® capsules.

Tables 24, 25, and 27 show data for percent deconned from 0 to 29 for ACL56 cores with GD and 0 to 41 with GB. Tables 25, 26, and 28 show data for 1-hr decon percentages from 57 to 75 for GD and 65 to 80 for GB with $Ca(OCl)_2$ cores. This data correlates with earlier studies that showed nonencapsulated $Ca(OCl)_2$ to be a more effective decon for GB (88%) and GD (78%) than for nonencapsulated ACL56 (see Table 8).

Capsule Leach Tests. Encapsulated decon applied on incapacitated personnel may contact body fluids such as blood or perspiration, or may otherwise be subjected to presence of liquid water or other aqueous media. It is believed that release of large quantities of the $-OCl^-$ core materials, especially into open wounds, would be generally undesirable. Consequently it was considered important to compare capsule samples for rate of leaching in water.

Ten capsule samples, previously evaluated with CWA, were selected for aqueous leach tests. These were 38388-5-1, -5-2, -7-2, -8-2, -10-2, and -18-1, each of which have calculated coating levels of 10% applied in the fluidized bed and 37984-19, -43, -46, and -48, each of which have calculated coating levels of 25% applied by phase separation. In this test, a weighed quantity of capsules (0.22 or 0.25 g) was placed in a beaker with 500 ml distilled water and stirred during the first hour. Aliquots (50 ml) were taken at 5 min, 30 min, 60 min, and 24 hr, as well as 48 and 72 hr tests for selected samples. These aliquots were analyzed for "available chlorine" (a standard measure of the $-OCl^-$ activity, i.e., available oxidizer). The 5-, 30-, and 60-min periods were chosen, based on the assumption that the decon capsules would usually be removed from treated, incapacitated personnel within an hour of their application. The 24-, 48-, and 72-hr tests were run to provide additional comparative data on these capsules.

TABLE 28. CWA-MICROCAPSULE EVALUATIONS: $Ca(OCl)_2$ PARTICLES ENCAPSULATED IN PARLON® S125 BY SPRAY DRYING COMPARED WITH CAB381-20 BY PHASE SEPARATION

$Ca(OCl)_2$ Particle Size um	Encapsulation Process	Wall Material %	Wall Material Type	5-Min Test Results[a] Hexane Wash %	5-Min Test Results[a] $CHCl_3$ Wash %	5-Min Test Results[a] Deconned %	60-Min Test Results[a] Hexane Wash %	60-Min Test Results[a] $CHCl_3$ Wash %	60-Min Test Results[a] Deconned %
With GD									
<74	Spray Drying	25	Parlon	90	13	[a]	35	8	57
45-74	Phase Separation	25	CAB	41	13	46	23	16	61
With GB									
<74	Spray Drying	25	Parlon	64	17	19	18	17	65
45-74	Phase Separation	25	CAB	11	27	62	5	16	79

[a] The % deconned is calculated by subtracting the sum of hexane wash % and $CHCl_3$ wash % from 100%. For these samples the sum of the wash % exceeded 100.

The analytical test used was titration with 0.1 N sodium thiosulfate solution in the presence of dilute sulfuric acid, potassium iodide, and starch. The various core materials used in preparing the selected capsule samples were separately analyzed. These were 300 to 595 μm ACL56, 300 to 595 μm $Ca(OCl)_2$, 150 to 300 μm $Ca(OCl)_2$, 74 to 150 μm $Ca(OCl)_2$ and 45 to 74 μm $Ca(OCl)_2$. For these core materials, 0.20 g samples were placed in 500 ml distilled H_2O and stirred for 5 min. Then 50 ml aliquots were titrated as for capsule samples. Table 29 shows test results with percent leached calculated by comparing ml sodium thiosulfate required for capsules to that required for the appropriate core material.

Contrary to expectations, the -8-2 (Butvar® polyvinyl butyral) and -7-2 (cellulose acetate butyrate) show better results than -10-2 (Saran®) or -5-2 and -5-1 (Parlon®). The latter two polymers are usually considered to be better water barrier materials than the other two. The $Ca(OCl)_2$ appears to leach more rapidly than the ACL56 (-18-1 compared to -5-1) for the fluidized bed coated samples. The fluidized bed CAB coated ACL56 showed slower leaching than the phase separation CAB coated ACL56 (38388-7-2 compared to 37984-19) although the latter has a (calculated) higher level of coating applied. The presence of DBDMH in the outer layer of capsule wall (-5-2 compared to -5-1) appears to increase the leaching rate during the first hour, as expected.

A comparison of capsules from runs 37984-43, -46, and -48 suggests that -43 and -46 (the two smallest sizes) were completely leached at 5 min, whereas -48 showed only 44% leaching. The fact that leach results for -43 and -46 did not appreciably increase after 5 min, though the numbers are 56% and 67% respectively, is interpreted to mean that these smaller capsules have undergone loss of activity during processing (encapsulation) and/or during storage.

The leach tests were terminated by 72 hours, at which time the -8-2, -7-2, and perhaps the -10-2 capsules were continuing to release. However, the low figures for these three at 72 hours may indicate that there has been some loss of activity during preparation or storage. Further evaluations, would be required to determine this and should include capsules with various coating thicknesses, such as 38388-7-1 and -7-3. This Phase I feasibility study was planned to determine a basic feasibility of the concept of using encapsulated $-OCl^-$ materials as decons, and was not intended to include a thorough evaluation of all significant properties of all of the capsules prepared.

Another series of aqueous leach tests was also run on capsule products from 38388-7-1, -7-2, and -7-3 which have calculated coating levels of 5%, 10%, and 15% respectively (weight basis). Table 30 shows the results of this test series. As expected, the percent leached at various times decreased with increasing capsule wall thickness. Past experience with fluidized bed encapsulation has shown that sometimes a rather sharp increase in coating effectiveness is observed at around 8% coating (capsule wall) with particles about 0.3 to 1.0 mm. Results obtained in these

TABLE 29. COMPARATIVE CAPSULE LEACH RATE EVALUATIONS[a]

Sample Number	Percent of Available Active Chlorine Titrated at Times of					
	Minutes			Hours		
	5	30	60	24	48	72
38388-8-2	0	1.4	1.4	26	39	47
-7-2	0	0.5	0.5	41	70	79
-10-2	2.1	12	20	59	68	70
-5-1	0	21	47	92	96	95
-5-2	8.8	59	82	84	--	--
-18-1	4.7	90	100	102	103	--
37984-19	48	106	110	109	--	--
-43	56	56	57	58	57	--
-46	67	70	69	72	71	--
-48	44	82	95	101	100	--

[a] Figures shown are percentages based on comparison of titrations of capsule leach liquor at times shown to solutions prepared from nonencapsulated corresponding materials in estimated equivalent quantities (i.e., based on 0.20 g core material in 500 ml distilled water).

TABLE 30. EFFECT OF WALL THICKNESS (% COATING) ON AQUEOUS LEACH TEST RESULTS[a]

	38388-7-1 (0.21 g)[b]	38388-7-2 (0.22 g)[b]	38388-7-3 (0.23 g)[b]
% CAB coating[b]	5	10	15
5-min leach	1.2%	0%	0%
60-min leach	53%	0.5%	0.5%
24-hr leach	93%	41%	21%
crushed[c]	not determined	97%	104%

[a]Figures shown are percent of core material leached based on 0.20 g core material (ACL56).

[b]Calculated percent coating. Actual percent coating probably somewhat less. Sample size used for analysis was based on this calculated percent coating to provide 0.20 g core material.

[c]Sample crushed with mortar and pestle, dissolved in water and analyzed.

tests appear consistent with that experience, with a much greater difference seen between -7-1 and -7-2 than between -7-2 and -7-3, especially at 60 min.

Among the capsules evaluated in the leach test, the 38388-8-2 (10% Butvar® coating on 300-595 μm ACL56 cores) and the 38388-7-2 (10% CAB coating on 300-595 μm ACL56 cores) show especially excellent results up to 60 min, and these low levels of $-OCl^-$ leached probably constitute a minimal hazard. Depending on the level of capsule application, the amount of fluids available, and $-OCl^-$ leach rate in these specific fluids, some of the other capsule systems may also provide adequate leach resistance. The very dilute, pure water leaching is probably more extreme than most actual conditions.

Skin Decon Experimentation Using Microencapsulated Decontaminants. Previous studies have indicated that the penetration behavior of a wide number of chemicals through pig skin is similar to that through human skin. Also, it has been demonstrated that there is a definite and reproducible relationship between the permeabilities of skins from different species.[4] Based upon these findings, pig skin was chosen for the skin decon phase of this study since it is extremely difficult to obtain cadaver skin samples. This change in the basic testing procedures was agreeable to the Sponsor. The skin samples were removed from a young pig with an intact layer of subcutaneous fat. The whole skin from the belly area was stored at -20^0 C.

Typically, diffusion cells are used in the measurement of chemical penetration through excised skin. In a previous study conducted at Battelle, a diffusion chamber was designed (see Figure 6) to study CWA penetration through excised pig skin and the effect of various decontaminants.

The chamber was designed to hold the sample taut by a stainless steel retaining ring on a Teflon® locking ring. The sample was suspended with an ultimate exposure area of 1.3 cm^2.

Prior to analysis, the skin sample was thawed and the subcutaneous fat removed using a surgical blade. The skin was draped over the sample locking ring, and the skin retainer was slipped into place to secure the sample. Excess skin was trimmed away from the ring. The locking ring and sample were slipped into the decontamination chamber with the fatty side of the sample resting on top of a stainless steel screen and held in place with a Teflon® ring.

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[4] Tregeor, R. T. Physical Function of Skin, Molecular Movement: The Permeability of Skin. New York: Academic Press, p. 1 (1966).

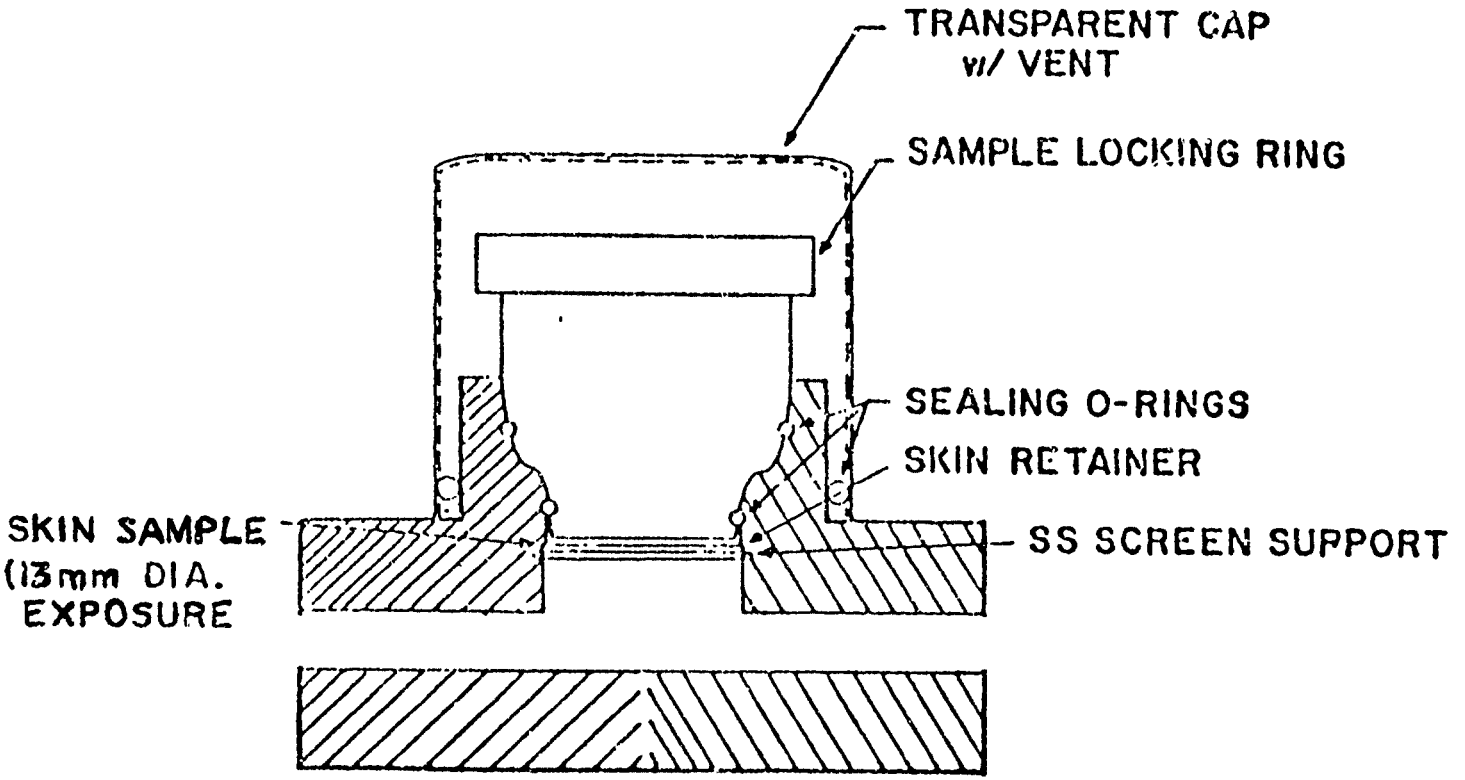

Figure 6. Diffusion Chamber.

The apparatus was transferred to a hood and the epidermis was spiked with 10 µl of neat agent. The agent was allowed to penetrate the sample for 5 min. A premeasured amount of decon was then applied covering the entire surface of the exposed skin. The apparatus remained undisturbed within the hood for an additional 30 min. The skin surface was then rinsed with hexane to remove the microcapsules and any residual neat agent. The rinses and microcapsules were collected in a beaker. The rinses were quickly decanted into a volumetric flask to minimize extraction of agent from the microcapsules. The rinse solution was diluted to volume and the amount of residual agent was later determined by gas chromatography.

The skin sample was ground in a homogenizer with hexane as the solvent and sonicated for 15 min to extract the penetrated agent. The solution was concentrated to 1 ml. The sample extract was fortified with an internal standard and subsequently analyzed by capillary gas chromatography/mass spectrometry. The individual chromatograms from these analyses are shown in Figures B1 to B16 in Appendix B.

Three types of control samples were analyzed. The first, a nondosed skin sample handled in the same manner as a test sample to determine the presence of any of interferring compounds. No interferences were detected (see Figure B-1).

The other controls consisted of skin samples dosed with neat agent followed by a 5- or 35-min wait. The controls were then handled as were the test samples. The 5-min delay sample was informational on the amount of agent that penetrated before application of a decon. The extent of penetration possible without decon added is evident with the 35-min exposure. These findings are listed in Table 31. As expected, the degree of penetration was proportional to the increase in exposure time.

All microcapsule samples tested showed decreases in penetrated agent percent at 35 min compared to controls. For example, the 38388-18-2 test shows only 5% agent penetrated at 35 min compared to 32% for control (and 1% for control at 5 min). Thus only an additional 4% penetrated after capsules were applied, compared to an additional 31% for the control. An anti-penetration effectiveness percentage was calculated from the data for penetrated agent (see Table 31) with percent anti-penetration effectiveness equal to $100\left(1 - \frac{\text{test sample} - \text{5-min control}}{\text{35-min control} - \text{5-min control}}\right)$. Figures greater than 100% anti-penetration effectiveness indicate that the percentage of penetrated agent is lower for the capsule test sample than for the 5-min control. These data imply that the capsules have not only deconned the skin surface but have also extracted some of the agent that had already penetrated into the skin when the capsules were applied.

TABLE 31. CONTROL AND DECONTAMINATION ANALYTICAL DATA[a] FOR PIGSKIN TESTS

Sample	Agent	Decon Wt (g)	Residual Agent (%)	Penetrated Agent (%)	Nonrecovered and Deconned Agent (%)	Anti-Penetration[b] Effectiveness (%)
5-min control	HD		77	1	22	-
35-min control	HD		35	32	33	-
38388-7-2	HD	0.4238	28	13	41	61
38388-5-2	HD	0.4425	10	9	81	74
38388-18-2	HD	0.4001	57	5	38	87
5-min control	GB		76	3	21	-
35-min control	GB		2	127	0	-
38388-18-2	GB	0.3110	30	17	53	89
37984-43	GB	0.3083	15	7	78	97
37984-48	GB	0.3021	16	3	81	100
5-min control	GD		81	21	0	-
35-min control	GD		63	41	0	-
38388-18-2	GD	0.3183	63	9	28	160
37984-46	GD	0.3192	14	5	81	180
37984-48	GD	0.3054	11	13	76	140

[a] Analysis was performed using gas chromatography or capillary gas chromatography/mass spectrometry (see page 81).

[b] Calculated from figures in the penetrated agent column as follows:

$$\% \text{ Anti-penetration Effectiveness} = 100 \left(1 - \frac{\text{test sample} - \text{5-min control}}{\text{35-min control} - \text{5-min control}}\right)$$

Figures greater than 100% indicate extraction of agent already penetrated when capsules were applied 5 min after agent was applied.

While the 38388-18-2 appears best of the three capsule samples tested in anti-penetration effectiveness for HD, the 38388-5-2 capsules performed better in decon effectiveness (agent destroyed).

The 38388-18-2 capsules contained DBDMH in the capsule wall and developed color with neat HD as described earlier in this report. Color was not observed in the skin test with these capsules and HD until capsules were washed off the skin test sample. However, the quantity of capsules applied formed a layer that was more than one capsule in thickness. Thus, capsules contacting skin and agent were obscured by other overlaying capsules. Yellow-colored capsules were observed when capsules were removed during the wash step (after 30 min of capsule contact with the HD contaminated skin sample).

Run 37984-48 capsules performed best in skin tests against GB, both in decon activity and in anti-penetration effectiveness, and prevented any additional penetration of agent after capsules were applied. With GB, all three types of capsules appear to extract GB from the skin sample, but only 37984-43 and 37984-48 show high-level decon activity.

Although time and money did not allow for replicate analyses, the data, even based on limited experimentation, are encouraging and do indicate that decontamination is probable with the proper microcapsule systems. A more extensive study is necessary to evaluate more precisely the efficiency of the microcapsules as decontaminants. Different parameters need to be varied to evaluate the effect upon the decons and replicate experiments need to be done with a statistical evaluation of the data. Some of the recommended parameters to vary are as follows:

- Exposure Time. The critical time for application of the decontaminants needs to be delineated.
- Temperature. The temperature of the skin sample needs to be varied to simulate variances of actual typical skin temperatures of real subjects in different field conditions.
- Application. The physical exertion used in application might affect the efficiency of the decontaminant; i.e., applied lightly versus impacting the decontaminant on the skin with force.
- Identification of Unknowns. There are unknown peaks identified in the different chromatograms shown in Figures B-3 to B-17. The peaks may be metabolites and should be analyzed to determine if they are toxic also.

APPENDIX A

PATENT REFERENCE LISTS A AND B

APPENDIX A

PATENT REFERENCE LIST A
MODERATELY RELATED PATENTS

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APPENDIX B

CHROMATOGRAMS FOR SKIN TEST STUDY

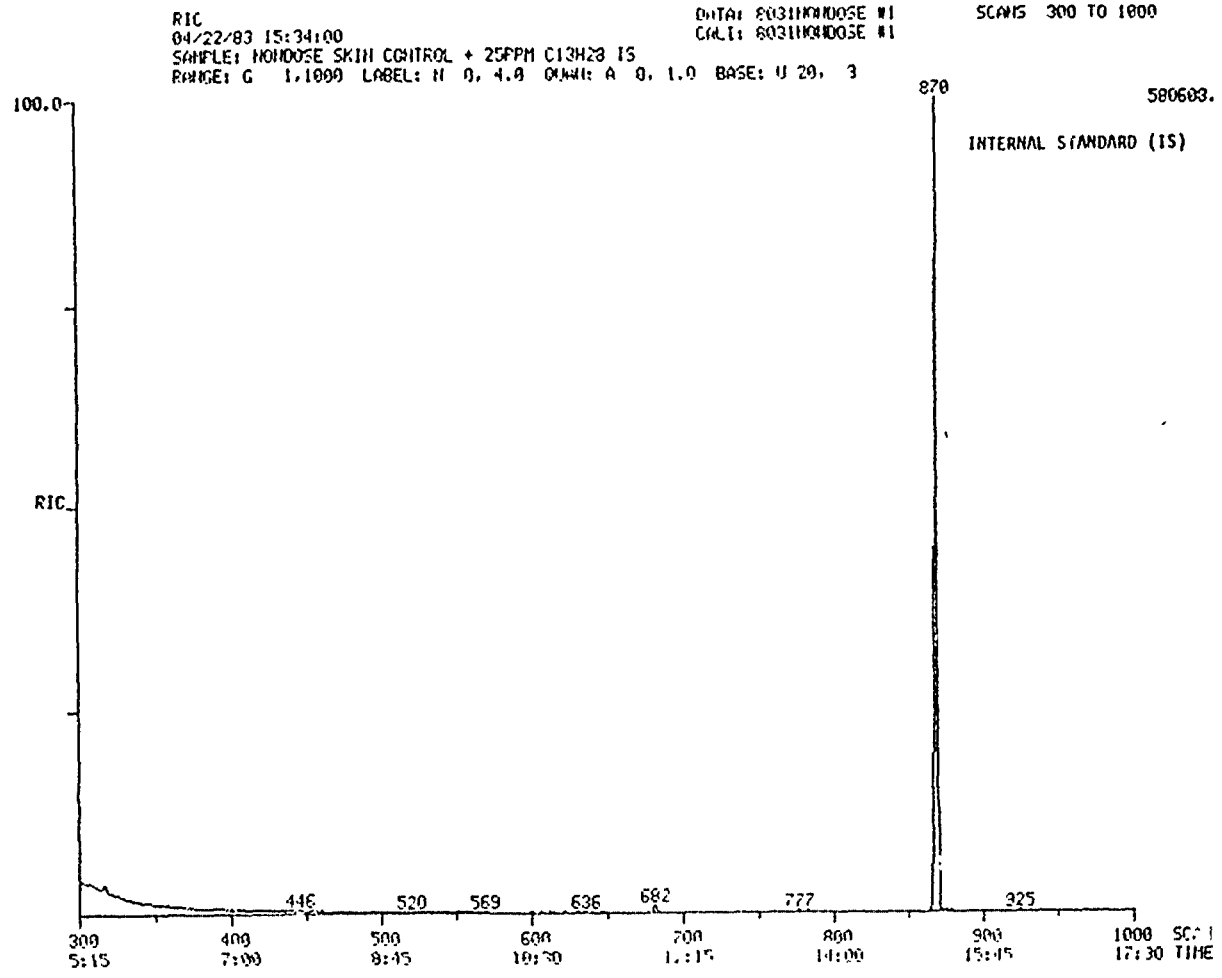

Figure B-1. Nondosed skin control.

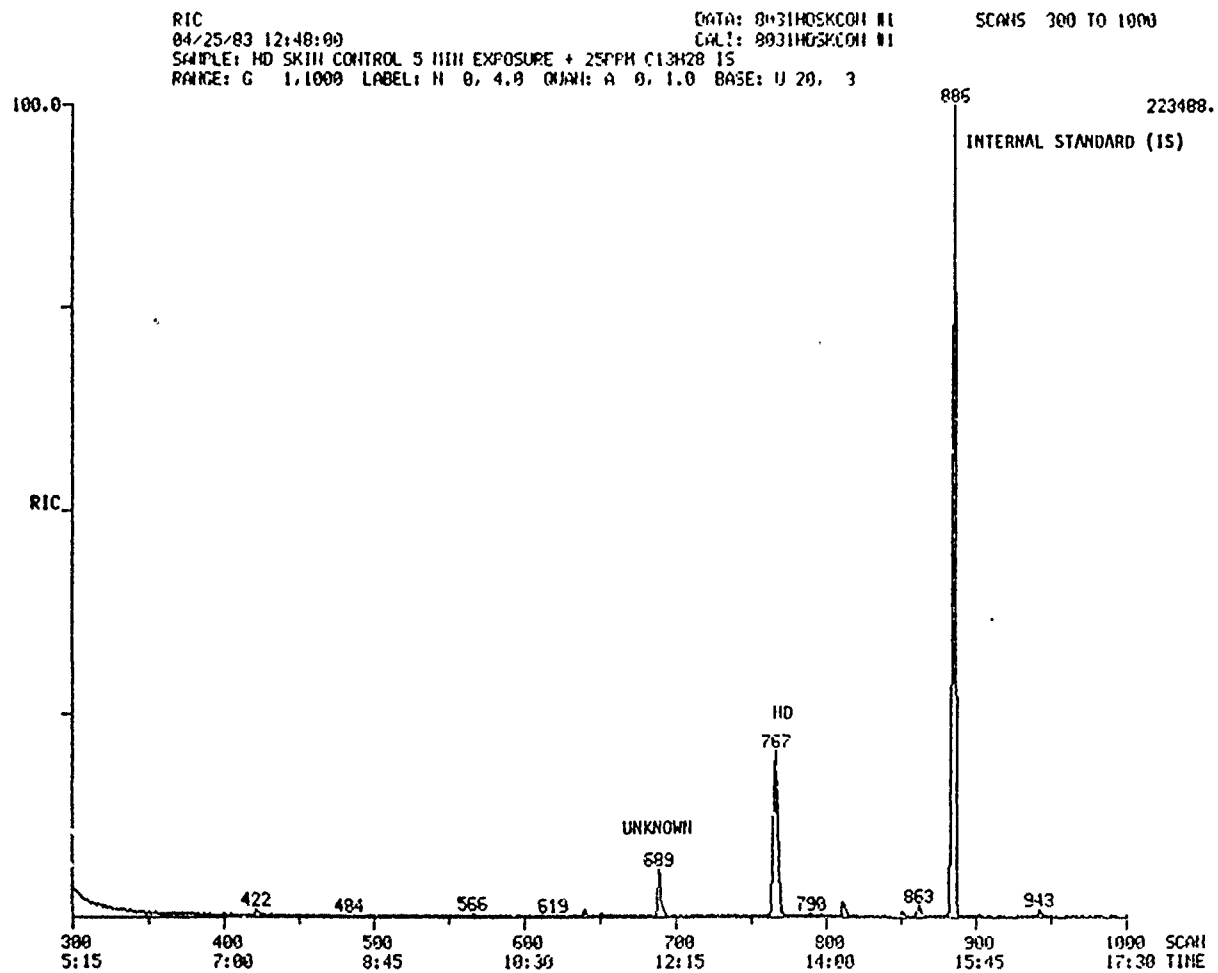

Figure B-2. HD skin control, 5-min exposure.

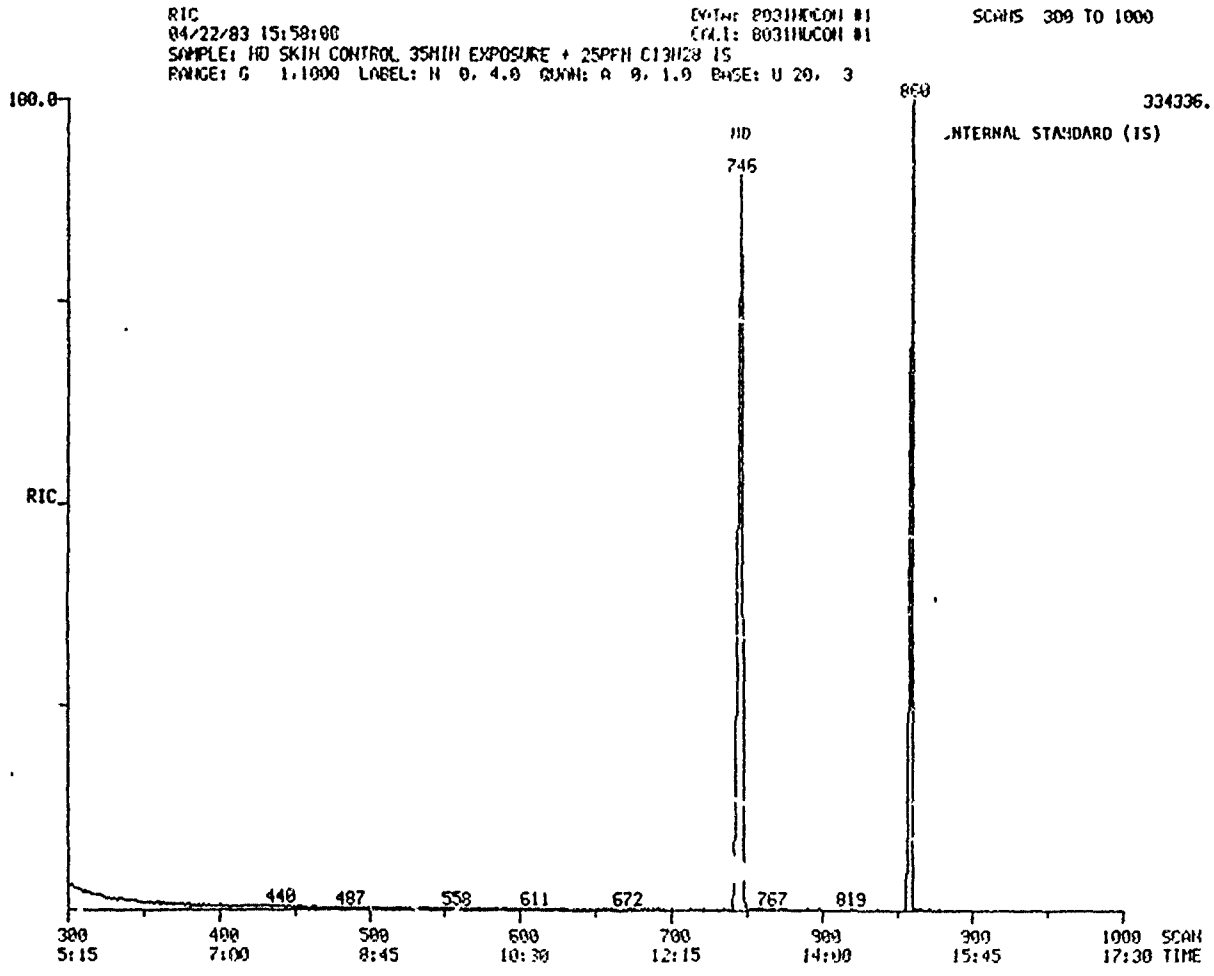

Figure B-3. HD skin control, 35-min exposure.

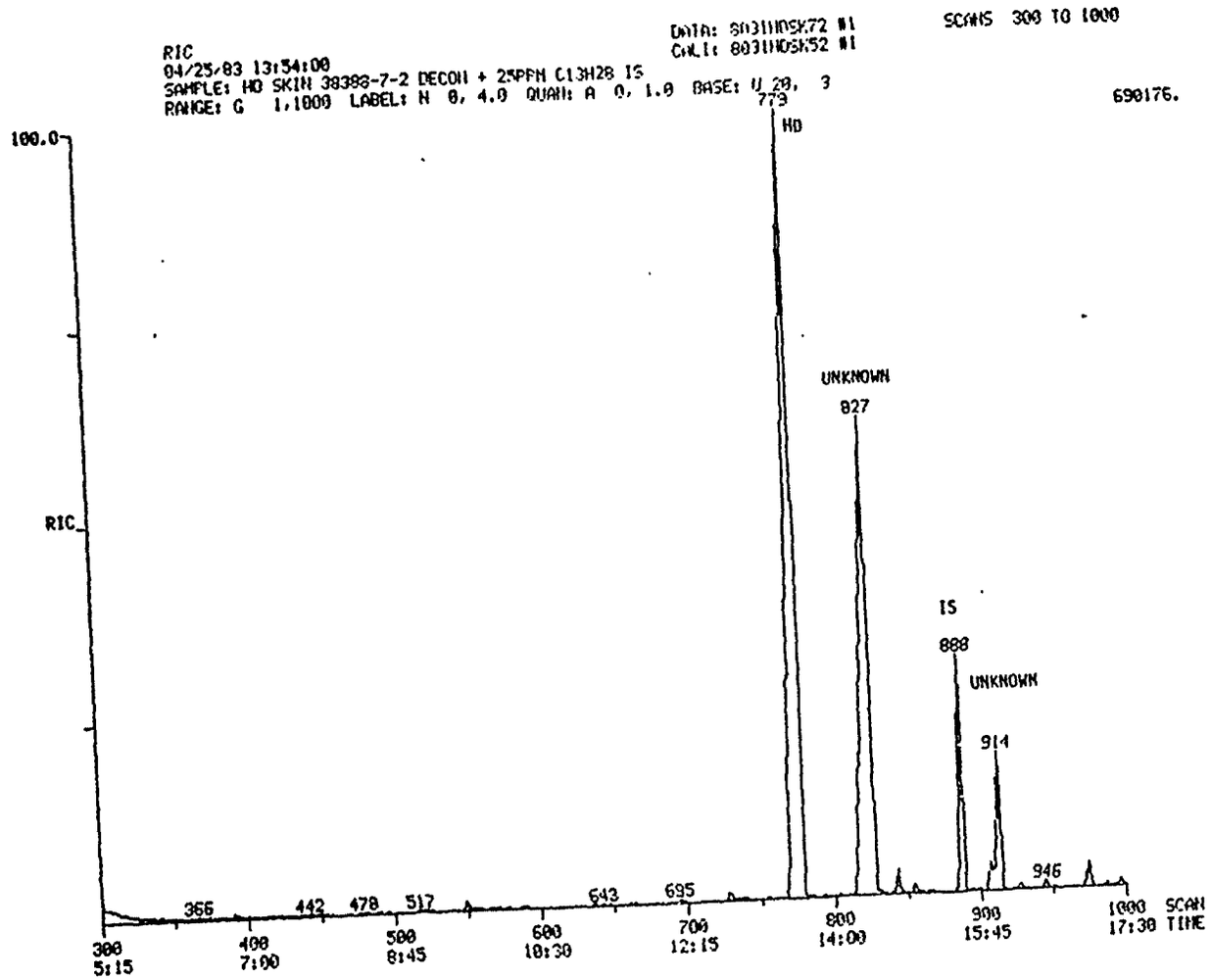

Figure B-4. HD with 0.4238 g 38388-7-2.

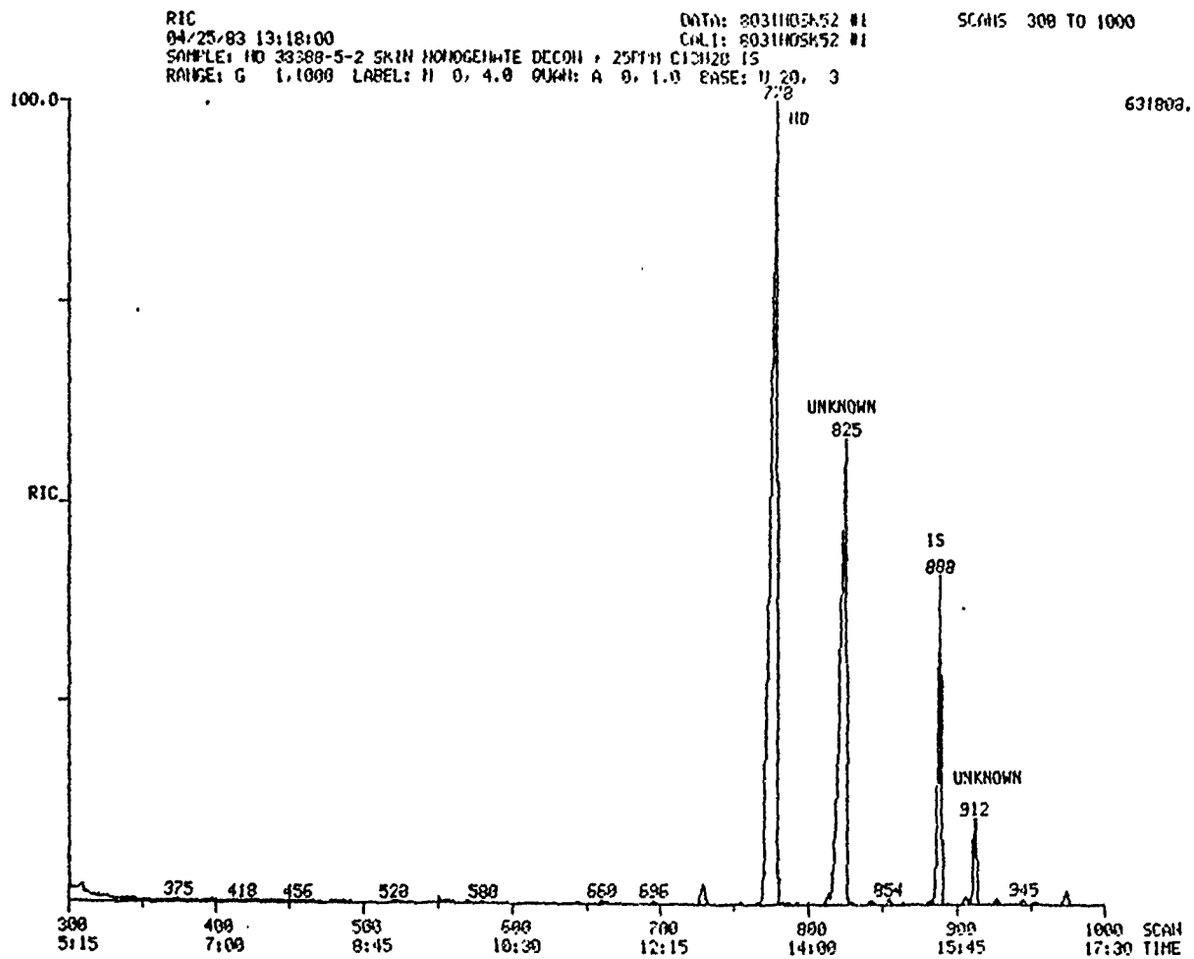

Figure B-5. HD With 0.4425 g 38388-5-2.

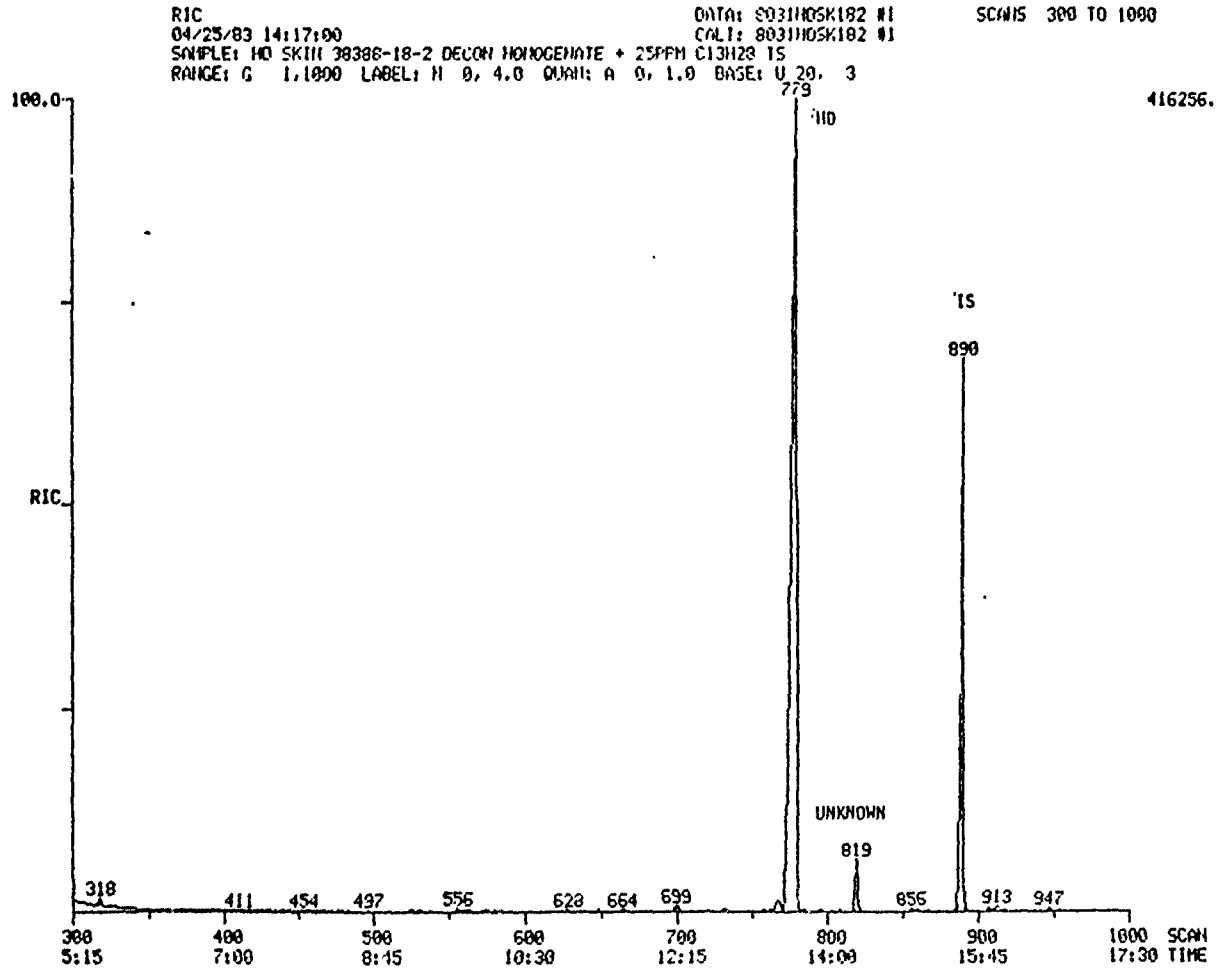

Figure B-6. HD with 0.4001 g 38388-18-2.

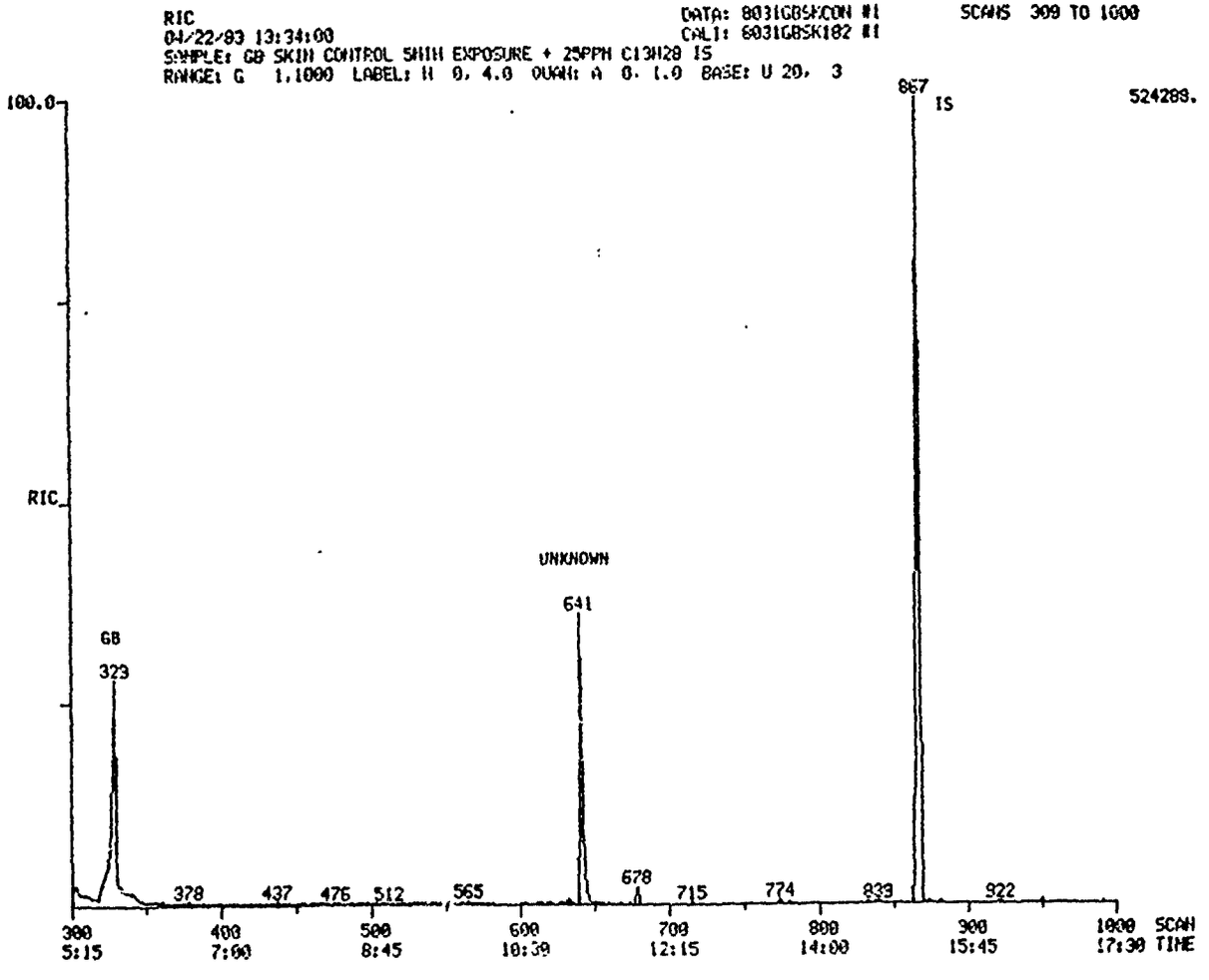

Figure B-7. GB skin control, 5-min exposure.

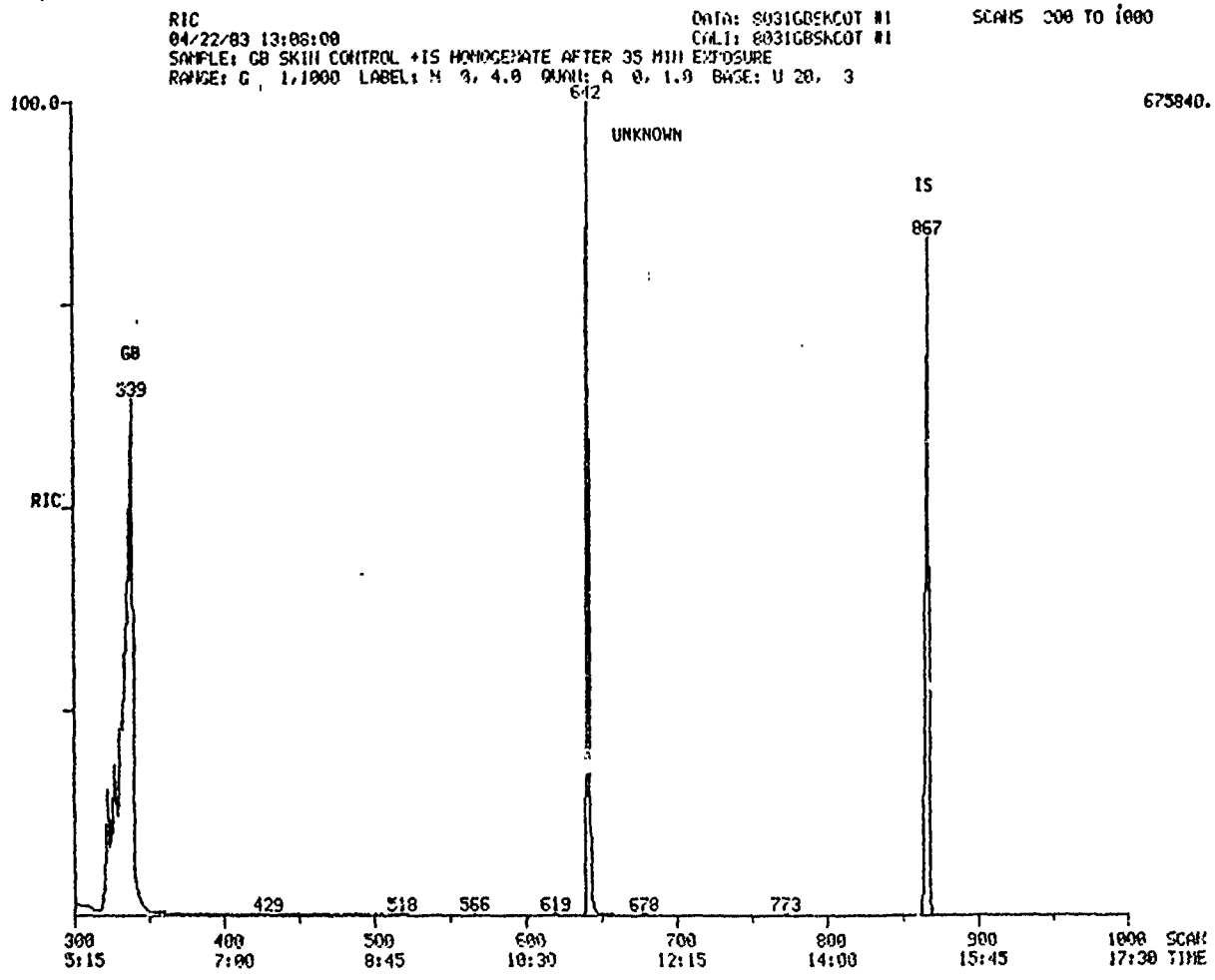

Figure B-8. GB skin control, 35-min exposure.

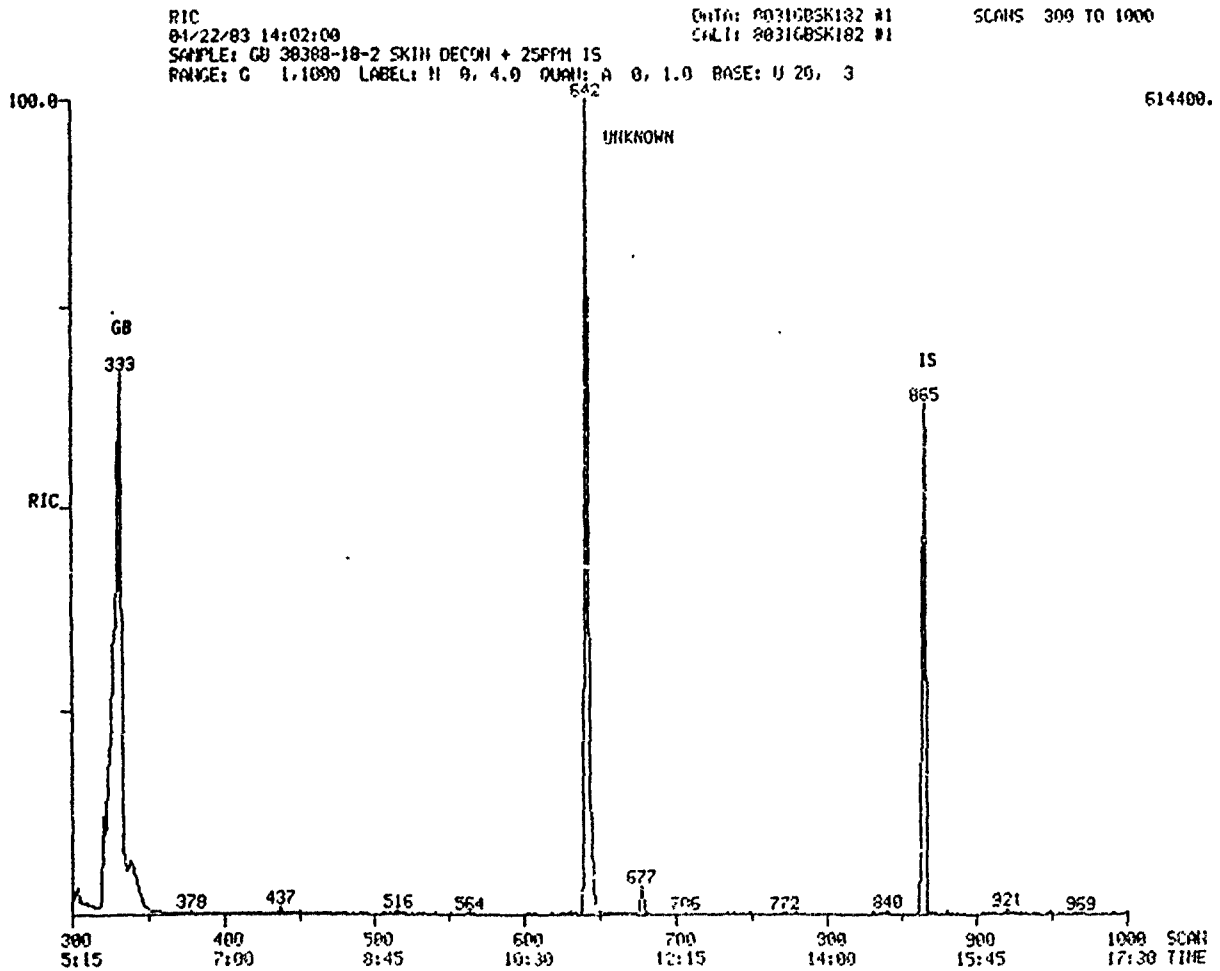

Figure B-9. GB with 0.3110 g 38388-18-2.

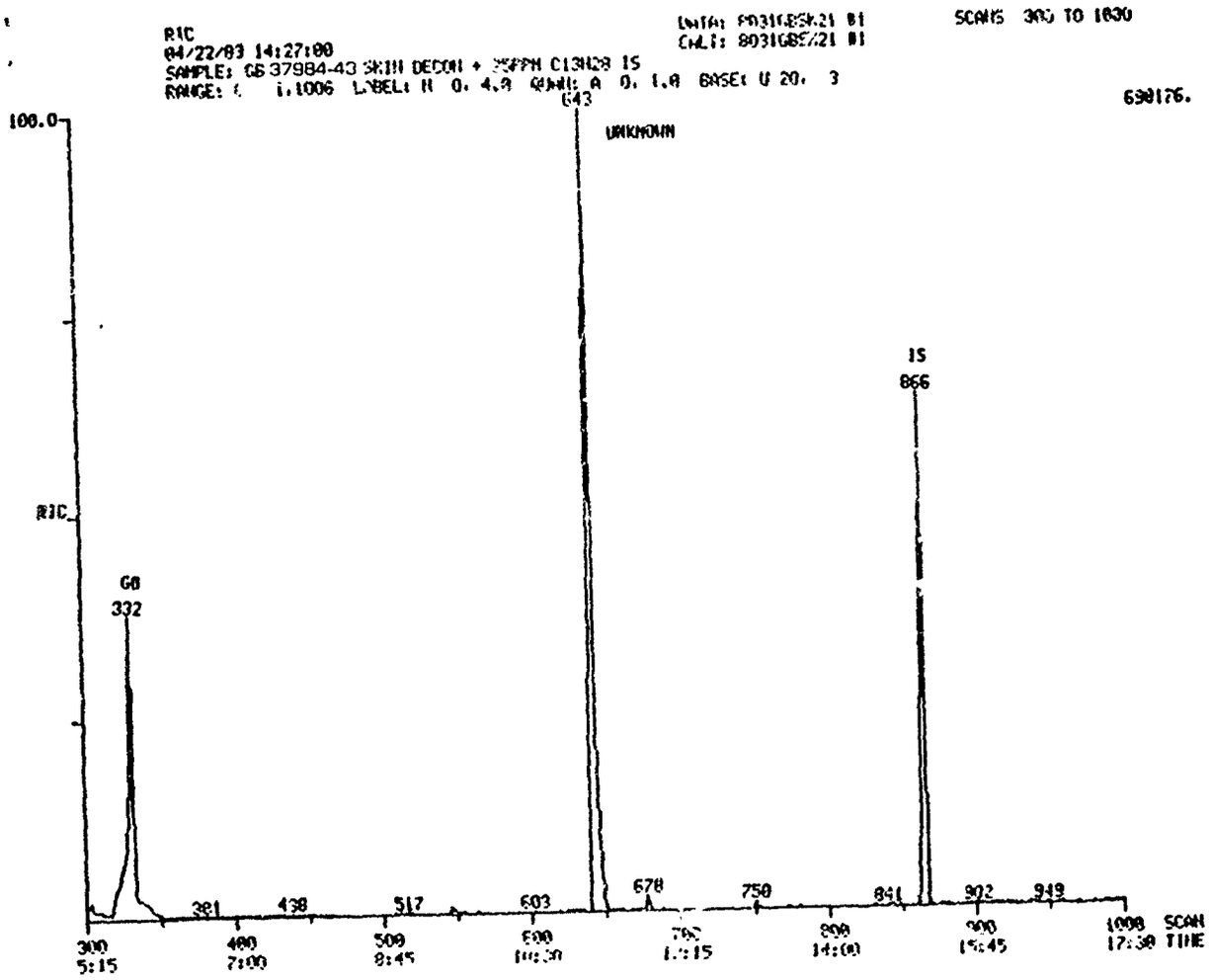

Figure B-10. GB with 0.3083 g 37984-43.

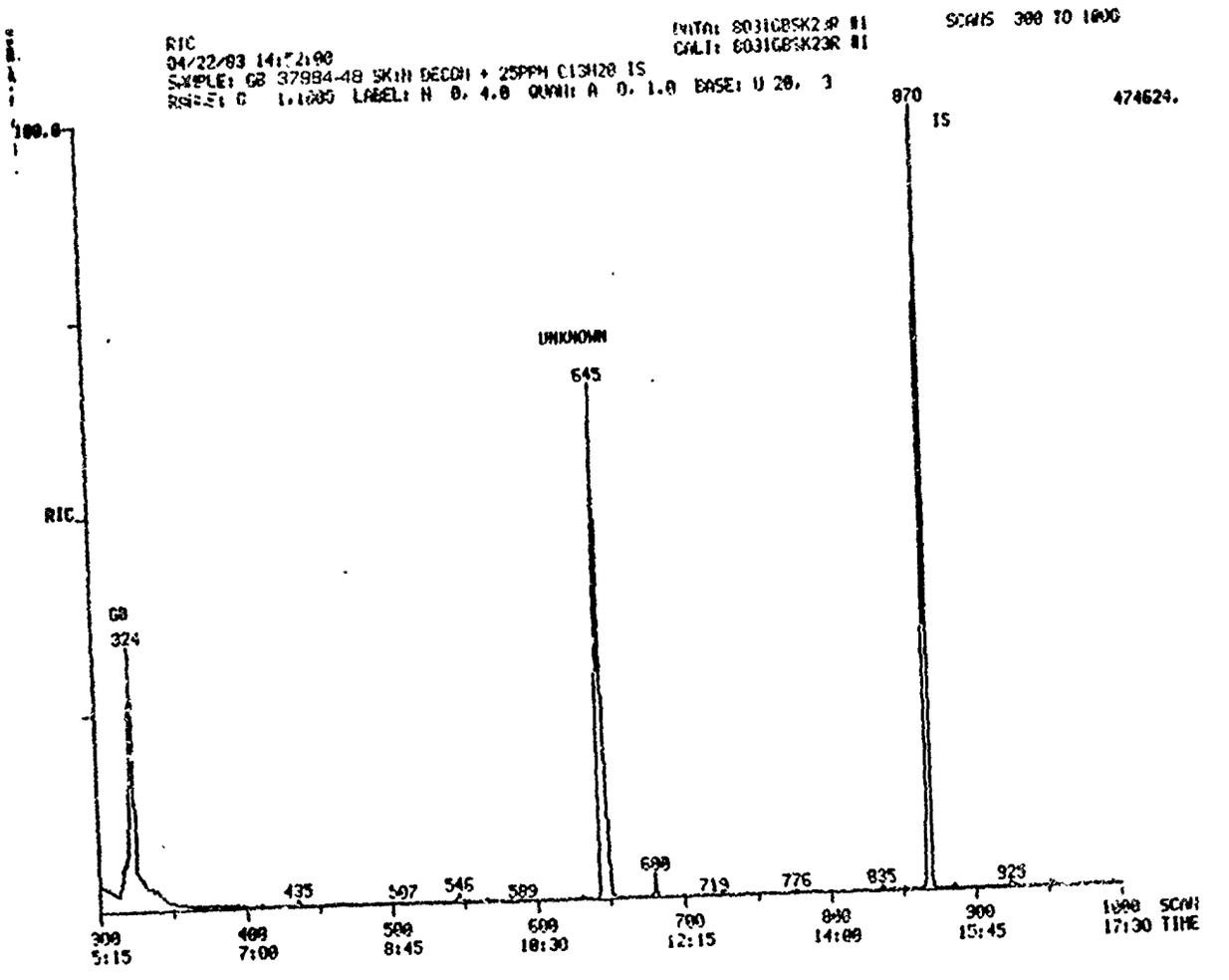

Figure B-11. GB with 0.3021 g 37984-48.

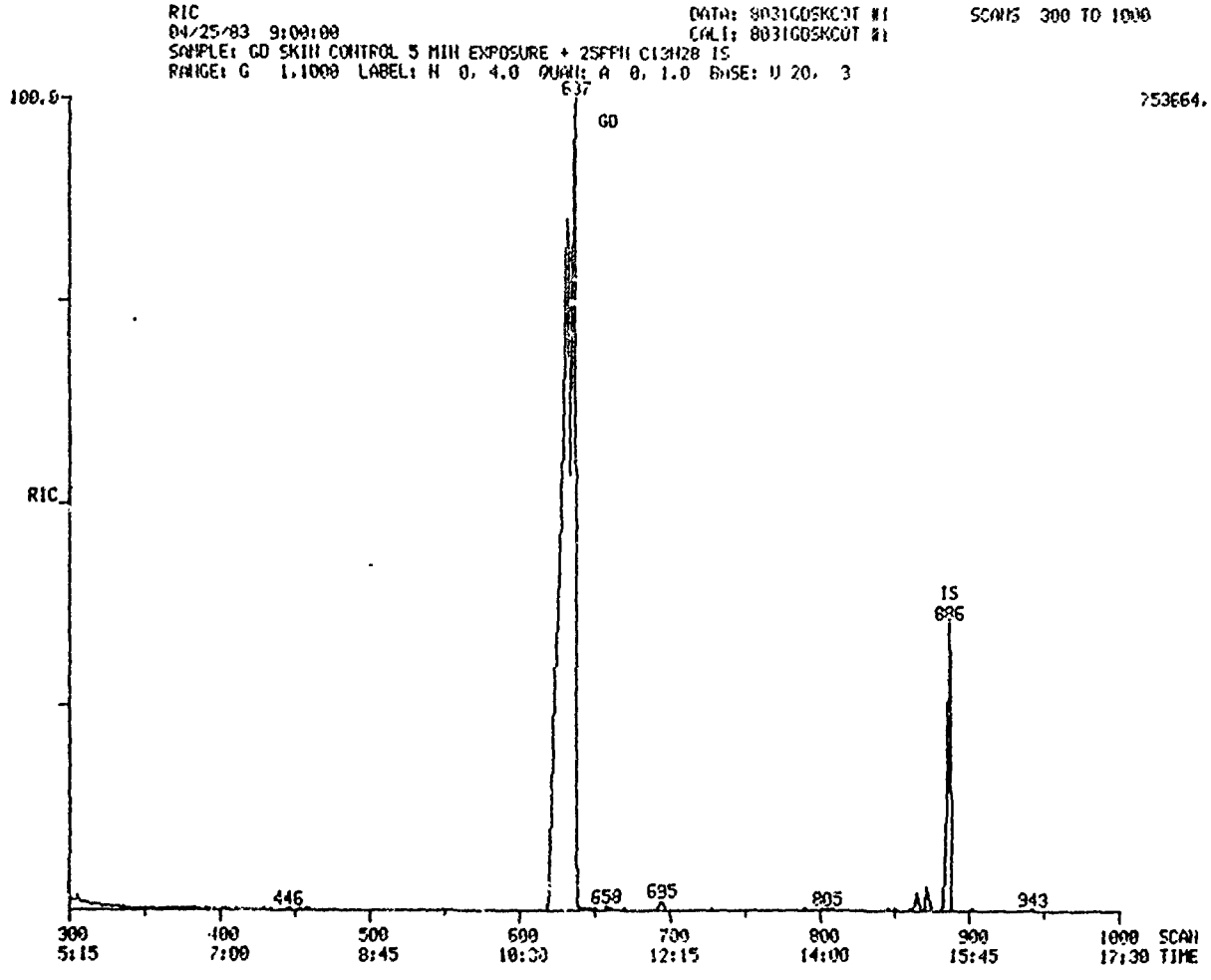

Figure B-12. GD skin control, 5-min exposure.

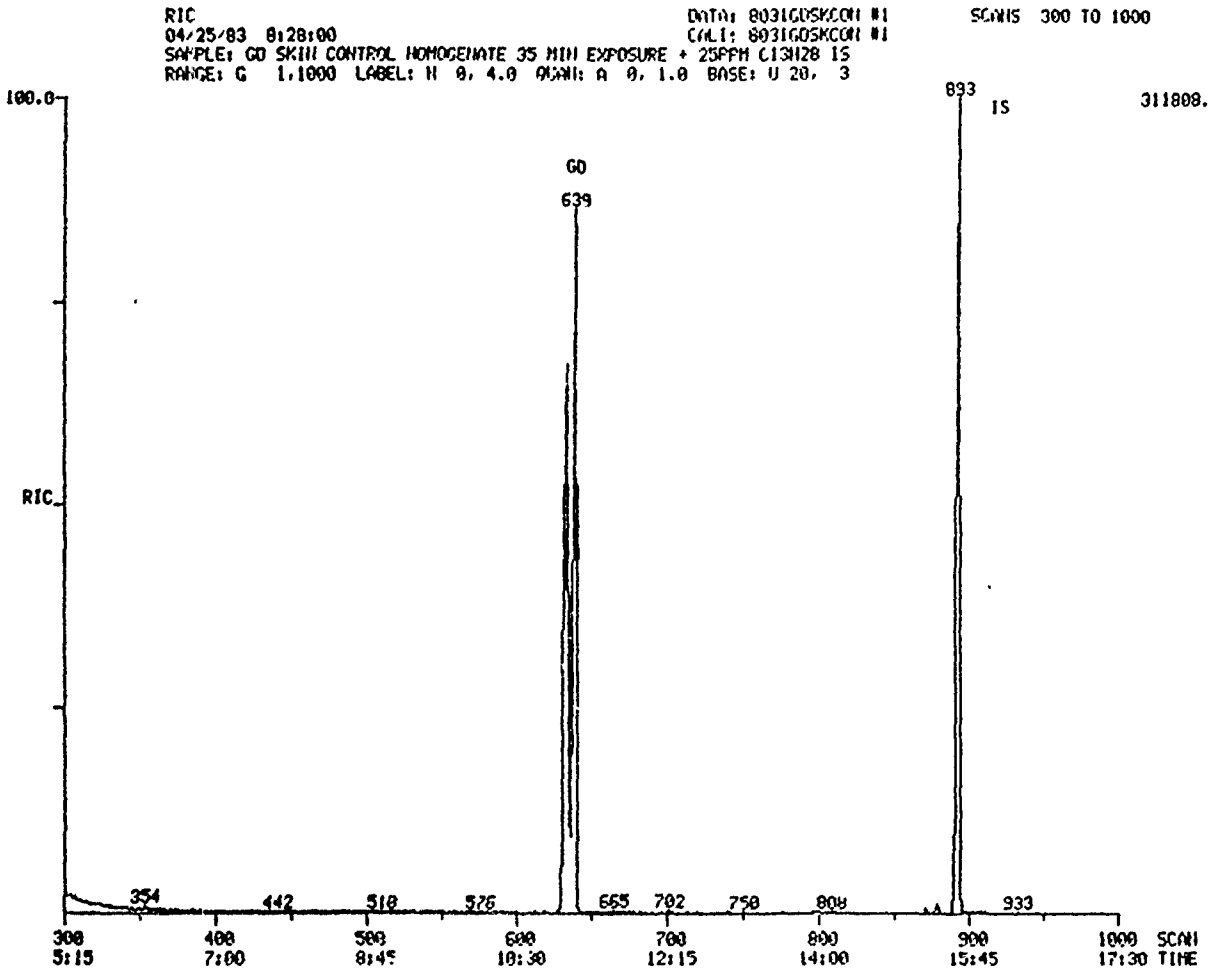

Figure B-13. GD skin control, 35-min exposure.

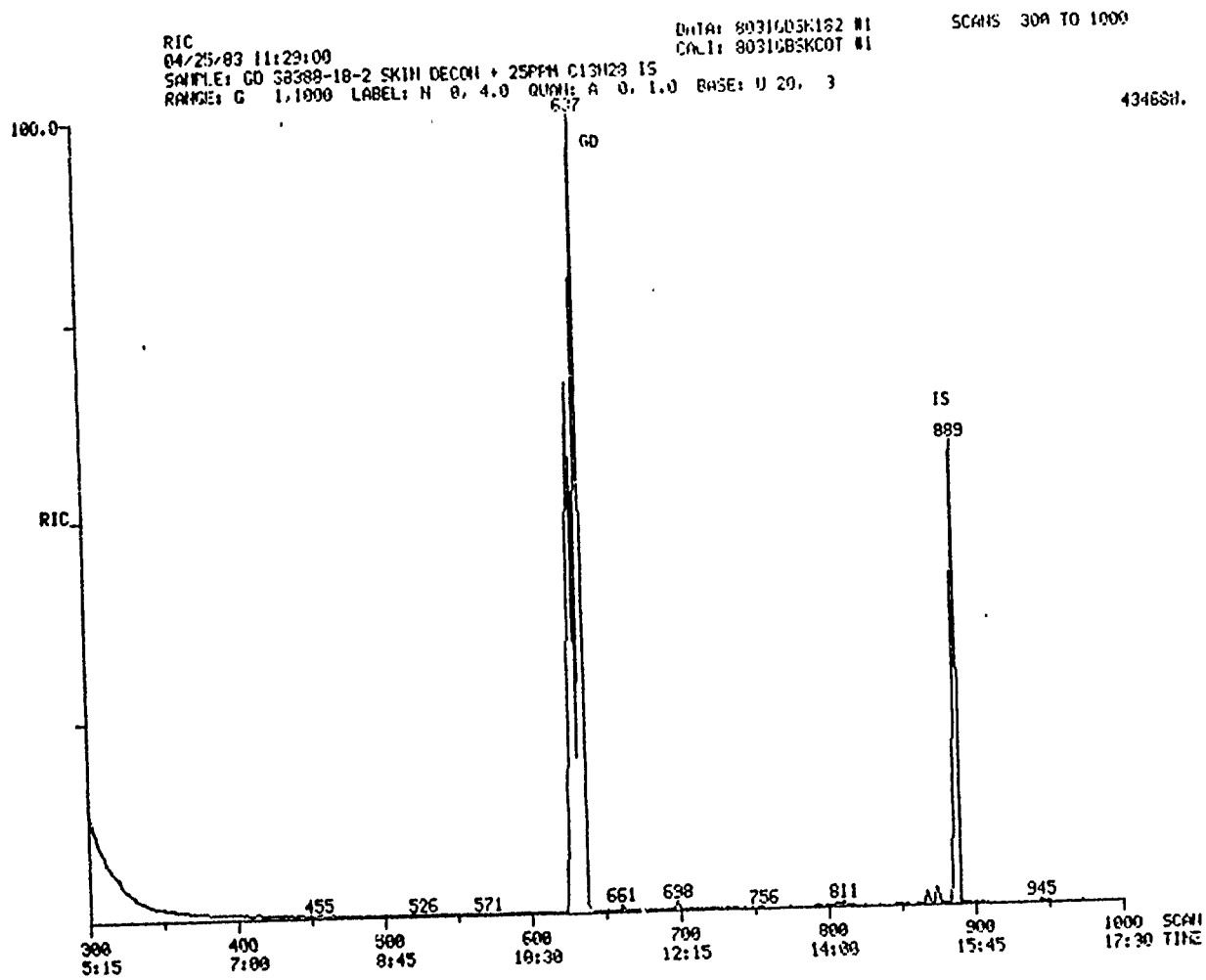

Figure B-14. GD with 0.3183 g 38388-18-2.

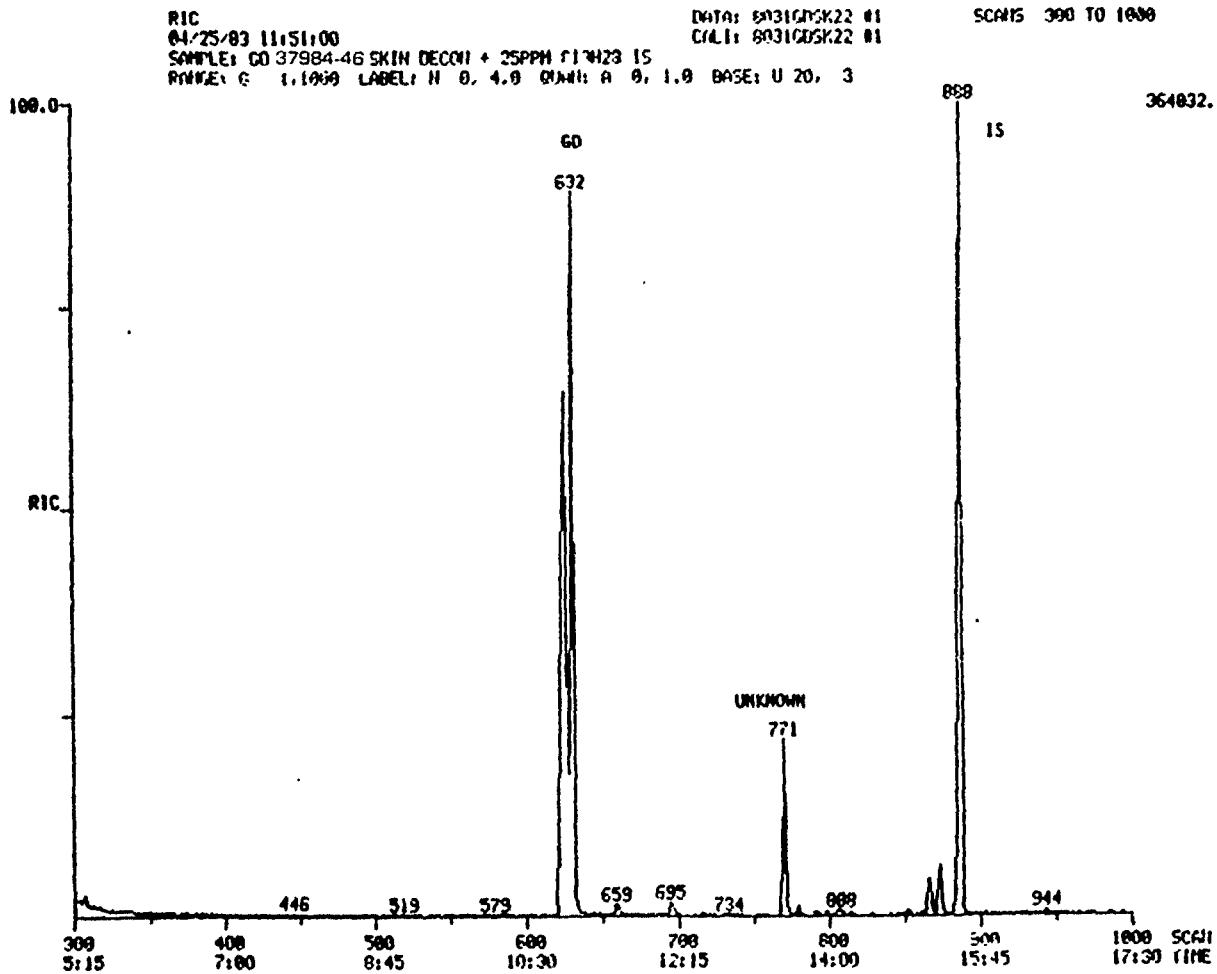

Figure B-15. GD with 0.3192 g 37984-46.

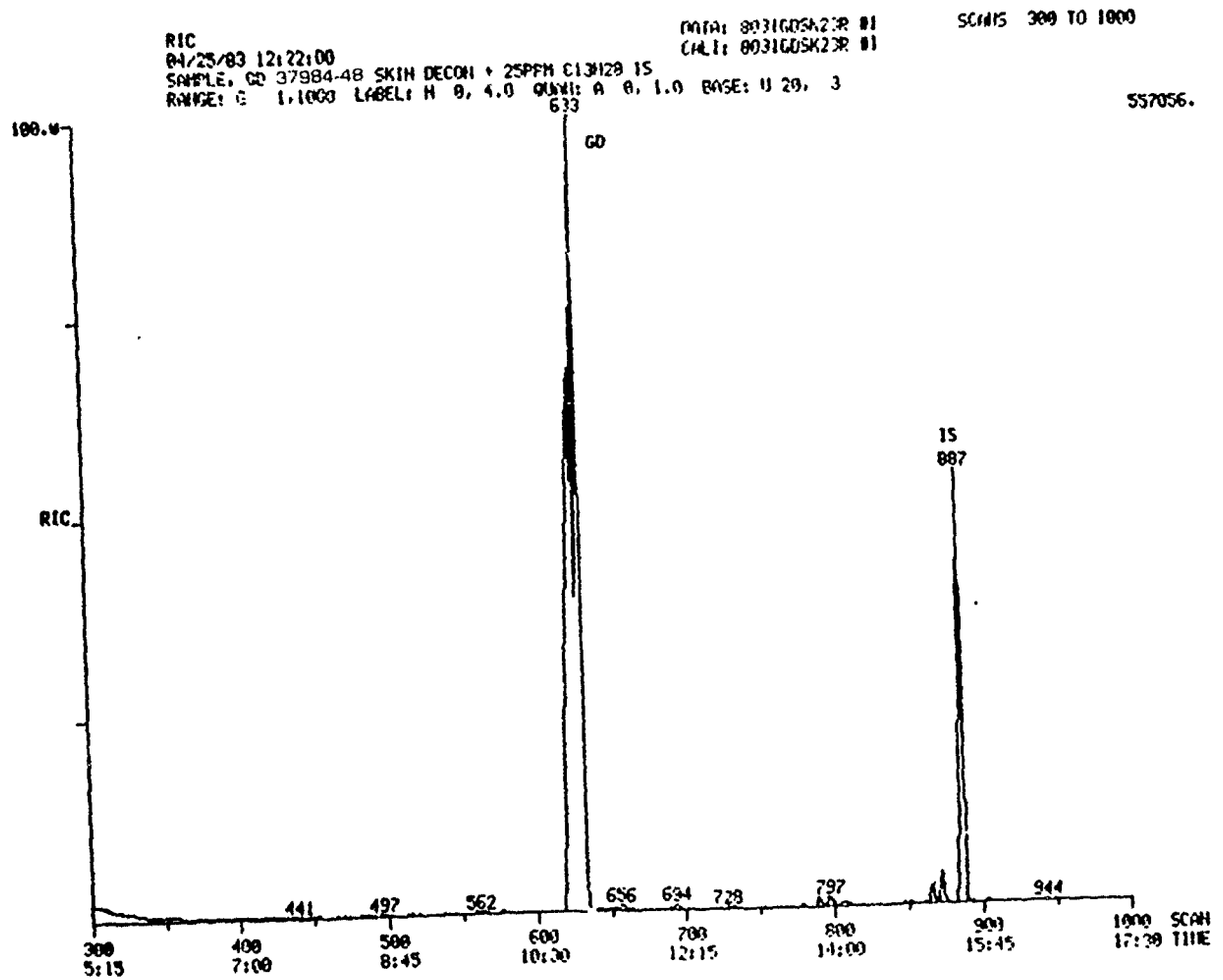

Figure B-16. GD with 0.3054 g 37984-48.